# VYSOKÁ ŠKOLA CHEMICKO-TECHNOLOGICKÁ V PRAZE Fakulta chemické technologie Ústav polymerů

Habilitační práce

Katalytické polymerace olefinů

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## PROHLÁŠENÍ

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## Poděkování

Poděkování patří mým studentům, kteří významnou měrou přispěli k velké části výsledků uvedených v této práci. Děkuji svým kolegům dr. Jiřímu Pinkasovi z ÚFCH JH AV ČR a doc. Milanu Erbenovi z FCHT Univerzity Pardubice za spolupráci v oblasti katalytických polymerací olefinů pomocí metalocenových komplexů. V oblasti polymerační děkuji za spolupráci prof. Cramailovi z Univerzity Bordeaux. Chci poděkovat i všem kolegům z ústavu polymerů za všestrannou pomoc a příjemné pracovní prostředí. Dík patří i pracovníkům sklářských dílen a centrálních laboratoří. Svým vedoucím děkuji za toleranci při volbě mých témat výzkumu. Škole děkuji za významnou podporu při vybavování laboratoří unikátními přístroji. Děkuji své ženě Ivaně za podporu a trpělivost.

#### Souhrn

Předkládaná habilitační práce shrnuje výsledky dosažené v naší laboratoři v oblasti katalytických polymerací olefinů. Největší pozornost je kladena na živé/řízené polymerace olefinů, které vedou k modelovým polyolefinům s řízenou molární hmotností a řízeným větvením. Tyto polymerace byly převážně prováděny pomocí diiminových komplexů niklu a palladia připravovaných rovněž v naší laboratoři. U těchto komplexů byl systematicky zkoumán vliv struktury diiminového ligandu na rozsah vedlejších reakcí a byly nalezeny nové deriváty, které umožňují řízenou polymeraci vyšších olefinů. Toto rozšíření knihovny diiminových ligandů vhodných pro přípravu komplexů umožňujícími živou polymeraci olefinů umožnilo i rozšíření intervalu, ve kterém je možno měnit větvení připravených polymerů neboť větvení je rovněž ovlivněno objemností substituentů. Dále byl pomocí UV-VIS spektroskopie studován mechanismus aktivace Ni diiminových komplexů a na základě terminačních experimentů navržena struktura částic odpovídající jednotlivých signálům spektra. Poprvé byly pro aktivaci živé koordinační polymerace pomocí Ni diiminových komplexů využity jednoduché organohlinité sloučeniny jako alternativa k nestabilnímu methylaluminoxanu, navíc v řádově nižším poměru Al/Ni. V dalších pracích bylo zkoumáno katalytické chování nových komplexů připravených ve spolupracujících laboratořích zaměřených na organometalickou syntézu. Takto byly zkoumány metalocenové komplexy Zr a Ti pro polymerace a kopolymerace ethylenu a polometalocenové komplexy Ti pro syndiospecifickou polymeraci styrenu.

#### Summary

The Thesis summarizes results of our laboratory in the field of catalytic olefin polymerizations. The most studied were living/controlled olefin polymerizations leading to tailor made polyolefins with controlled molar mass and controlled branching. These polymerizations were predominantly catalyzed by nickel and palladium diimine catalysts which were also prepared in our laboratory. For these complexes we systematically investigated the effect of ligand structure on the extent of side reaction. New derivatives allowing living polymerization of higher olefins were found. This extension of library of diimine ligands suitable for the preparation of complexes capable of living olefin polymerization allowed also the broadening of the interval in which it is possible vary the branching of prepared polyolefins as the branching is dependent on the bulkiness of diimine ligands. Mechanism of activation of Ni diimine complexes was studied by UV-VIS spectroscopy and the spectra signals were assigned to structures of discrete species. For the first time it was shown that living olefin polymerization can be achieved by Ni diimine complexes activated by simple organoaluminium compounds instead of instable methylalumoxane, moreover in much lower Al/Ni ratio. Metallocene complexes of Zr and Ti prepared in collaborating laboratories were investigated in ethylene polymerization and copolymerization and Ti half-metallocenes were investigated in syndiospecific styrene polymerization.

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## 1. Úvod

V současné době polyolefiny, tj. zejména polyethylen a polypropylen, představují více než 50% produkce všech syntetických plastů. Nejvýznamněji produkované typy polyethylenu a všechny polyolefiny odvozené z vyšších olefinů je možno polymerovat na vysokomolekulární produkty pouze koordinační (katalytickou) polymerací. Při iontové nebo radikálové polymeraci totiž dochází k tvorbě stabilních allylových radikálů nebo iontů, které způsobují intenzivní přenos na monomer mající za důsledek vznik pouze oligomerních produktů.

Nejrozšířenějšími katalyzátory pro koordinační polymerace olefinů jsou Zieglerovy katalyzátory na bázi halogenidů titanu v kombinaci s alkylaluminiovými kokatalyzátory, které umožňují jak přípravu lineárního polyethylenu (HDPE)<sup>1</sup> tak přípravu izotaktického polypropylenu<sup>2</sup>. Významnou skupinou katalyzátorů pro výrobu HDPE jsou i komplexy na bázi oxidů chromu vyvinuté firmou Phillips Petroleum Company<sup>3</sup>.

Výzkumu katalyzátorů byla od jejich objevu věnována značná pozornost a v průběhu let 1955-1980 byly vyvinuty 4 generace klasických heterogenních Zieglerových katalyzátorů. Na konci 70. let 20. st. byla Kaminskym a Sinnem objevena schopnost účinné aktivace homogenních katalytických systémů na bázi metalocenových sloučenin (obsahujících cyklopentadienylové cykly ve struktuře ligandu a kovy 4.-6. skupiny) pomocí methylaluminoxanu (MAO)<sup>4, 5</sup>. Tyto homogenní katalytické systémy jsou vysoce aktivní a někdy jsou označovány jako Zieglerovy katalyzátory 5. generace. Vzhledem k jejich rozpustnosti v reakčním prostředí poskytují jeden typ růstových center (single-site) a polyolefiny pomocí nich připravované mají úzkou distribuci molárních hmotností. Od 90. let 20. st. došlo dále k rozvoji homogenních katalyzátorů neobsahující cyklopentadienylové ligandy, tzv. postmetalocenových katalyzátorů<sup>6</sup>, často založených na kovech z 8.-10. skupiny<sup>7</sup>.

Pro přípravu speciálních typů polymerů, jako jsou blokové kopolymery, hvězdicovité polymery nebo koncově funkcionalizované polymery je využíváno metod tzv. živé/řízené polymerace, tj. takové polymerace, kde je potlačen nevratný přenos a terminace. První katalytický systém pro živé/řízené kooordinační polymerace olefinů byl objeven až v roce 1979<sup>8</sup>, kdy již byly živé iontové polymerace rutinně využívány<sup>9</sup>. K většímu rozvoji živých koordinačních polymerací došlo zejména v 90. letech 20. st. v souvislosti s rozvojem nemetalocenových katalyzátorů. Z tisíců homogenních komplexů dosud připravených umožňuje živou/řízenou koordinační polymeraci olefinů jen asi 15-20 skupin komplexů<sup>10,</sup> <sup>11</sup>. Jednou z nich jsou diiminové komplexy niklu a palladia objevené Brookhartem<sup>12-15</sup>, které jsme se zabývali v pracích [**P1-P6**]. Vedle schopnosti řídit molární hmotnost vznikajících polyolefinů umožňují díky unikátnímu mechanismu polymerace, tzv. "chain walking" (CW) mechanismu, i přípravu větvených polyolefinů. CW představuje konkurenční reakci k propagaci a jeho poměr k propagaci lze ovlivňovat

strukturou katalyzátoru, koncentrací monomeru a reakční teplotou<sup>16</sup>. Palladnaté diiminové komplexy vykazují velmi extenzivní CW a umožňují tak přípravu hypervětvených polyolefinů<sup>17, 18</sup>.

Již zmíněné metalocenové katalyzátory patří mezi nejaktivnější homogenní katalytické systémy pro polymeraci olefinů<sup>19</sup>. Strukturně se jedná o komplexy nesoucí dva cykopentadienylové (Cp) cykly (nebo větší kondenzované cykly s Cp strukturním motivem jako je indenyl nebo fluorenyl) koordinované k centrálnímu kovu<sup>20</sup>. Typicky se jedná o Cp<sub>2</sub>MX<sub>2</sub> komplexy, kde M je nejčastěji Zr, Ti nebo Hf a X jsou typicky halogenidové nebo alkoxy skupiny. Cp kruhy mohou být substituovány alkylovými či arylovými skupinami a vzájemně mohou být propojeny můstky, což vede k zafixování polohy ligandů centrálního kovu, které je důležité v případě asymetrických komplexů při přípravě stereoregulárních polymerů. Nejaktivnější zirkonoceny mají při polymeraci ethylenu aktivitu v řádu 10<sup>4</sup> kg PE na 1 g Zr. Na aktivitu zirkonocenu má zásadní vliv substituce Cp ligandu a typ X skupin, které jsou při aktivaci MAO zčásti substituovány alkylovou skupinou (tvorba vazby kov-uhlík nezbytná pro inserci olefinu) a zčásti abstrahovány za vzniku volné koordinační vakance nutné pro koordinaci olefinu. V práci P7 jsme se zabývali vlivem substituce Cp ligandů v zirkonocenech a titanocenech na jejich katalytické chování při polymeraci ethylenu. Práce P8 byla zaměřena na studium odstupujících ligandů X titanocenů při polymeraci ethylenu a jeho kopolymeraci s norbornenem, která vede ke vzniku amorfních kopolymerů (cyclic olefin copolymers COC), jejichž teplota skelného přechodu je ovlivněna množstvím zabudovaného cyklického monomeru.

Komplexy obsahující pouze jeden Cp kruh jsou nazývány polometaloceny a největší uplatnění nalézají při stereospecifické polymeraci styrenu<sup>21</sup>. Radikálově polymerovaný styren poskytuje amorfní polystyren s vlastnostmi vhodnými jen pro výrobu základních polymerních výrobků, na které nejsou kladeny nároky na zvýšenou pevnost a tepelnou odolnost (např. kelímků). Koordinační polymerace s vhodnými katalyzátory naopak umožňuje přípravu tzv. syndiospecifického polystyrenu sPS, který, díky pravidelnému uspořádání fenylových substituentů podél polymerního řetězce, může vytvářet krystalickou fázi s teplotou tání kolem 270°C, vysokou chemickou odolností a dobrými mechanickými vlastnostmi. sPS tak představuje speciální polyolefin na rozhraní konstrukčních a high-performance polymerů. Polometalocenovými komplexy Ti a jejich polymeračním chováním jsme se zabývali v pracích **P9 a P10**.

## 2. Komentář k předloženým publikacím

### 2.1 Živé koordinační polymerace olefinů pomocí $\alpha$ -diiminových komplexů Ni a Pd

Až do roku 1995 sloužily komplexy s niklem jako centrálním kovem pouze jako katalyzátory pro oligomeraci olefinů a další reakce pro přípravu nízkomolekulární látek<sup>22</sup>. Využitím stericky objemných α-diiminových ligandů v komplexech niklu a palladia byly pomocí těchto komplexů poprvé získány vysokomolekulární polymery<sup>12</sup>. Odlišnost funkce těchto katalyzátorů spočívá v bránění β-H eliminaci stíněním axiálních poloh komplexu, které jsou potřeba pro tvorbu přechodového stavu β-H eliminační reakce<sup>7, 23</sup>. α-diiminové komplexy Ni a Pd navíc vedle propagační (inserční) reakce katalyzují i tzv. "chain walking" reakci, která vede k migraci kovového centra zpět do řetězce a vede ke vzniku větvených polymerů<sup>23-25</sup>. Krátce po objevu těchto katalyzátorů bylo zjištěno, že komplexy s objemnými ligandy umožňují natolik potlačit přenosové reakce, že umožňují tzv. živou polymeraci olefinů<sup>14, 15</sup>. V dalším vývoji byly syntetizovány i asymetrické komplexy Ni, které umožňují živou a zároveň isospecifickou polymeraci α-olefinů<sup>26, 27</sup>.

Studiu  $\alpha$ -diiminových komplexů věnovali v pracích [**P1-P6**] a zaměřili se na studium vlivu objemnosti substituentů diiminového ligandu na živost polymerace, tj. na rozsah přenosových a terminačních reakcí. Objemnost substituentů zároveň určuje poměr propagační reakce a CW reakce a ovlivňuje tedy i stupeň větvení vznikající makromolekuly. V pracích **P1** a **P2** jsme se věnovali vlivu kosterních substituentů R<sub>1</sub> (Obr. 1) a v pracích **P3** a **P4** arylovým substituentům R<sub>2</sub> a R<sub>3</sub>. Práce **P5** a **P6** jsou zaměřeny na možnost řízení morfologie vznikajících polymerů pomocí micelárních katalyzátorů na bázi  $\alpha$ -diiminových komplexů Ni.



Obr. 1 Substituční polohy  $\alpha$ -diiminových komplexů niklu a paladia

#### *Vliv kosterních substituentů na živost polymerace [P3, P4]*

V práci [P1] isme syntetizovali sérii 4 komplexů Ni a Pd lišících se kosterními substituenty  $R_1$  (obr. 1) a zkoumali vliv reakčních podmínek na živost/řízenost polymerace hex-1-enu. Publikace<sup>13</sup> uvádí, že živá polymerace je omezena teplotou pod -10°C a koncentrací monomeru do 1 mol.l<sup>-1</sup>. Z našich výsledků vyplývá, že pro Ni komplex (R<sub>2</sub>=iPr, R<sub>3</sub>=H, R<sub>1</sub>=1,8-naftalendiyl) aktivovaný MAO je možno dosáhnout živé polymerace hex-1-enu i při teplotě +20°C. Dále při 0°C stejný katalytický systém umožnil přípravu polyhexenu s velmi úzkou distribucí molární hmotnosti i při koncentraci hex-1-enu 5.8 mol.l<sup>-1</sup> (disperzita Đ<1.30) i když při koncentraci vyšší než 2.8 mol-l<sup>-1</sup> již dochází k vzrůstu dispersity. O řízenosti polymerace rovněž svědčila lineární korelací mezi experimentálními a teoretickými hodnotami molární hmotnosti. Objemnost ligandu rovněž velmi výrazně ovlivňovala větvení polyhexenů, v případě Ni komplexů byly získány polyhexeny se 89 až 116 větvemi, což odpovídá přeuspořádání monomerních jednotek z 30-45%. Výrazný vliv na větvení polymeru má i volba centrálního kovu. Detailní <sup>13</sup>C NMR analýza ukázala na rozdíl v mikrostruktuře polyethylenu a polyhexenů připravených pomocí Ni a Pd katalyzátorů. Na rozdíl od PE, v jehož struktuře jsou zastoupeny všechny typy větví od C1 do C6 a delší větve, se ve struktuře polyhexenů vyskytují pouze methylové, butylové a delší větve. Paladnaté komplexy navíc mají výrazný obsah delších větví v důsledku vyššího rozsahu CW reakce. Pro tato pozorování bylo navrženo mechanistické schéma zahrnující 1,2 a 2,1-inserci a následné přeuspořádání řetězce v důsledku CW reakce.

Ni komplex (Obr. 1, R<sub>2</sub>=iPr, R<sub>3</sub>=H, R<sub>1</sub>=1,8-naftalendiyl), který poskytoval polyhexeny s nejužší distribucí molární hmotnosti byl rovněž podroben kinetické studii. Zkoumán byl zejména vliv koncentrace hex-1-enu na rychlost polymerace, kdy v literatuře byly známy práce, ve kterých byl pozorován záporný řád reakce vzhledem ke koncentraci monomeru<sup>28, 29</sup>. Přestože při jedné hodnotě počáteční koncentrace monomeru je závislost ln[M]<sub>0</sub>/[M] na čase lineární, což svědčí o reakci prvního řádu ke koncentraci monomeru, byl ze závislosti logaritmu polymerační aktivity na logaritmu koncentrace monomeru získán externí řád reakce -0,3. Toto chování bylo vysvětleno tvorbou růstových center s odlišnou reaktivitou, která je dána charakterem inserční vazby nikl-uhlík. CW reakcí po prvotní 2,1-inserci se vytváří lineární alkylový řetězec vázaný na Ni centrum. Takto vytvořené reakční centrum je reaktivnější než centrum nesoucí větvený alkyl vznikající 1,2-insercí. Poměr těchto center je ovlivněn koncentrací monomeru, která ovlivňuje CW. Reaktivnější růstová centra, tvořená přeuspořádáním pomocí CW reakce, vznikají ve větším podílu při nízkých koncentracích monomeru a celková reaktivita se tak při poklesu koncentrace monomeru zvyšuje.

V práci [**P1**] bylo rovněž poprvé pozorováno, že polyhexen s velmi úzkou distribucí molární hmotnosti lze připravit i pomocí Ni komplexu s menším kosterním substituentem R<sub>1</sub> (R<sub>2</sub>=iPr, R<sub>3</sub>=H, R<sub>1</sub>=methyl).

Studiu vlivu velikosti kosterních substituentů jsme se detailně věnovali v práci [**P2**]. V této práci jsme fixně zvolili isopropylové ortho-aryl substituenty a v R1 polohách byly diiminové ligandy substituovány vodíkovými atomy, methylovými skupinami, 1,2-butandiylovou nebo 1,8naftalendiylovou skupinou (Obr. 2). Z ligandů byly vytvořeny niklové komplexy, které byly po aktivaci MAO testovány při polymeraci hex-1-enu a propenu.



Obr. 2 Ni diiminové katalyzátory použité v práci [P2]

Při polymeraci hex-1-enu všechny komplexy při -10°C poskytovali polyhexeny s úzkou distribucí molárních hmotností naznačující živý charakter polymerace. Komplex **4** však vedl jen k velmi nízkému výtěžku polymeru. Komplex **2** poskytoval polyhexen s velmi úzkou distribucí molární hmotnosti i při 25°C avšak při použití komplexu **1** za těchto podmínek se výrazně snížila konverze hex-1-enu a distribuce molárních hmotností získaného polyhexenu se výrazně rozšířila.

Pro osvětlení průběhu polymerace byla provedena kinetická studie polymerace hex-1-enu. Koncentrace monomeru byla sledována pomocí GC odebraných vzorků reakční směsi. Díky této metodě se podařilo odhalit, že polymerace je doprovázena isomerací hex-1-enu na vnitřní hexeny (hex-2-en, hex-3-en), které polymerují podstatně pomaleji. Podobné chování bylo pozorováno zatím jen u Pd systémů<sup>15</sup>, v případě Ni diiminových komplexů isomerizaci před námi zatím nikdo nepopsal. Právě isomerace se u komplexu **1** a za vyšších teplot ukázala jako hlavní důvod nízkého výtěžku polyhexenu a GC ukazuje téměř úplnou přeměnu hex-1-enu na vnitřní hexeny. Při polymeraci hex-1-enu katalyzované komplexem **4** docházelo k intenzivní isomerizaci monomeru již při -10°C, kdy veškerý hex-1-en byl spotřebován během 1h. Z konverzních křivek byl dále u komplexu **1** patrný mírný pokles v koncentraci vnitřních hexenů během polymerace, doprovázený nárůstem výtěžku polymeru. To naznačuje, že i vnitřní hexeny mohou být pomalu inserovány do polymerního řetězce.

Živost polymerace, naznačená nízkými hodnotami disperzit molární hmotnosti, byla dále ověřována u komplexů **1** a **2** pomocí reiniciačních testů, kdy po spotřebování monomeru byl přidán jeho další podíl (stejné množství) a byla sledována změna molární hmotnosti. Při -10°C polymerace

iniciovaná oběma komplexy pokračovala za zhruba zdvojnásobení molární hmotnosti a zachování úzké distribuce, což ukazuje na zachování většiny růstových center. Živost polymerace dále potvrzoval i lineární narůst molární hmotnosti s konverzí monomeru. I při 25°C, kdy dochází u komplexu **2** k izomeraci 15-20% hex-1-enu, vykazovala polymerace hex-1-enu lineární závislost molárních hmotností na konverzi hex-1-enu na polymer (hex-1-en spotřebovaný na izomeraci nebyl uvažován).

Rozsah izomeračních reakcí je ovlivněn i kvalitou používaného kokatalyzátoru MAO, kdy bylo ukázáno, že při experimentech s použitím déle (~2 roky) skladovaného MAO dochází při polymeracích hex-1-enu pomocí komplexu **1** k asi 5-10% poklesu ve výtěžku polymeru a zároveň vzniká více vnitřních hexenů.

Celkový obsah větví polyhexenů připravených pomocí komplexů **1-3** se měnil od 100-160 větví/1000 C atomů. U komplexu **1** byly získány nejvyšší hodnoty blížící se teoretické hodnotě větvení získané **1,2**-insercí hex-**1**-enu (vedoucí k butylovým větvím) zdánlivě naznačující jen malý rozsah CW mechanismu. Detailní studium mikrostruktury polymerů pomocí <sup>13</sup>C NMR ovšem ukázalo na rozsáhlé změny ve struktuře polymeru ve všech polyhexenech připravených pomocí komplexů **1** a **3**. Vedle butylových větví byly u všech polyhexenů identifikovány i methylové větve a větve C6 a delší, což je běžným důsledkem CW mechanismu. Neočekávaně však polyhexen připravený pomocí **1** obsahoval i ethylové a propylové větve. Jako vysvětlení pro jejich přítomnost byla navržena inserce hex-**2**-enu (propylová větev) a hex-**3**-enu (ethylová větev). Modelovou polymerací hex-**2**-enu pomocí **1** byla ověřena přítomnost vysokého podílů propylových a methylových větví, pozorovány byly ovšem i ethylové a butylové větve, což ukazuje na významný vliv CW procesu i v případě polymerace vnitřních hexenů.

Komplexy **2**, **3** a **4** poskytly rovněž vysokomolekulární polypropyleny s úzkou distribucí molární hmotnosti naznačující možnosti živé polymerace i v případě propenu jako monomeru. Získané polymery byly rovněž výrazně přeuspořádané a oproti teoretické hodnotě 333 větví/1000 C atomů (v případě pravidelné 1,2- nebo 2,1-inserce) poskytly polypropyleny s 200-300 větvemi/1000 C atomů.

### Vliv o-arylových substituentů na živost polymerace [P3, P4]

V pracích [**P3**] a [**P4**] jsme se zabývali vlivem objemnosti ortho-arylových substituentů na řízenost polymerací olefinů katalyzovaných diiminovými komplexy niklu. V tomto případě byl jako kosterní ligand zvolen fixně 1,8-naftalendiyl a jako arylové substituenty byly využity methylové, ethylové, isopropylové a tert-butylové skupiny (Obr. 3). V práci [**P3**] byl detailně zkoumán vliv reakčních podmínek v širokém rozsahu reakčních teplot (-10 až 25°C) a poměrů monomeru k Ni iniciátoru (200-3200) s cílem odhalit limity objemnosti o-arylových substituentů, při kterých by již neprobíhala polymerace olefinů řízeně. U komplexů **3** a **5**, u nichž byly živá polymerace již známa<sup>13</sup>, bylo ověřeno, že polymerace hex-1-enu vede k produktu s predikovatelnou molární hmotností i při 25°C do poměru monomer/iniciátor<800. Vyšší koncentrace monomeru se projevovala mírným rozšířením distribuce molární hmotnosti v důsledku přenosu na monomer. Komplexy **7** a **8** s methylovými ortho arylovými substituenty umožňovali řízenou polymeraci hex-1-enu při poměru monomer/iniciátor<800 při teplotách nižších než 0°C. Komplex **9** s ethylovými substituenty inicioval řízenou polymeraci hex-1-enu za všech podmínek, tj. i při 25°C a až do poměru monomer/iniciátor<3200, kdy bylo možno tímto poměrem nastavit molární hmotnost v rozsahu 20 – 220 kg/mol s dispersitou do 1.1. Zároveň polymerace za různých koncentrací monomeru a reakčních teplot umožňují měnit větvení polyhexenu v intervalu 84-148 větví/1000 C atomů řetězce.

Živost polymerace hex-1-enu iniciované komplexy **8** a **9** dále dokládá lineární závislost molární hmotnosti na konverzi monomeru, lineárn závislost  $\ln[M_0]/[M_t]$  na čase a reiniciační testy, které prokázaly zachování všech růstových center po celou dobu polymerace.

Dále byla pomocí všech komplexů iniciována i polymerace propenu, při které se ukázalo, že méně objemný monomer vyvolává výraznější podíl přenosových reakcí a že komplexy **7** a **8** s methylovými skupinami poskytují produkt s výrazně rozšířenou distribucí molární hmotnosti, která se výrazně liší od teoretických hodnot. Komplex **9** potvrdil svou výjimečnou schopnost řízení polymeraci a poskytl polypropylen s velmi úzkou distribucí molárních hmotností.

U vybraných polyhex-1-enů jsme studovali pomocí <sup>13</sup>C NMR detailně i jejich mikrostrukturu ve vztahu k mechanismu polymerace. Nejvýraznější přeuspořádání struktury polyhexenového řetězce způsobené CW mechanismem bylo pozorováno pro mono-tert.butyl substituovaný komplex **2**, který rovněž poskytl polyhexen s nejvyšším poměrem methylových/butylových větví, což dále indikuje vysoký rozsah CW procesu. Překvapivě u polyhexenu připraveného pomocí komplexu **4** byly detekovány i propylové a ethylové větve, které se v ostatních polyhexenech nevyskytovaly. Jako vysvětlení byla navržena možnost inserce hex-1-enu do méně stíněných sekundárních Ni-C vazeb. Alternativním vysvětlením by však také mohl být vznik vnitřních isomerů, pozorovaný později u komplexů s méně objemnými kosterními substituenty diiminového ligandu [**P2**], a jejich následné zapojení do polymerního řetězce.



Obr. 3 Ni diiminové katalyzátory použité v pracích [P3, P4]

V navazující práci [**P4**] jsme se zaměřili na možnosti aktivovat diiminové komplexy niklu (Obr. 3) pomocí jednoduchých organohlinitých sloučenin namísto MAO a na živost jimi iniciovaných polymerací hex-1enu. Vedle vyšší ceny MAO a nutnosti jej využívat v řádově vyšším nadbytku je hlavní motivací hledání jeho náhrady jeho nestabilita v roztoku při skladování, která vede k nereprodukovatelnosti výsledků polymerací. Pomocí komplexu **5** byl nejprve proveden screening aktivačních schopností diethylaluminiumchloridu (DEAC), ethylaluminiumdichloridu (EADC), dimethylaluminiumchloridu DMAC) a methylaluminiumdichloridu (MADC) při polymeraci hex-1-enu. Ethyl deriváty, DEAC a EADC, vykázaly podobnou polymerační aktivitu jako MAO, methyl deriváty během zvoleného polymeračního času nedosáhly úplné konverze monomeru. Kromě **5**/DMAC ostatní systémy poskytly polyhexen s úzkou distribucí molární hmotnosti a počet polymerních molekul vztažených na 1 molekulu Ni komplexu byl blízký hodnotě 1, což ukazuje na dobrou účinnost všech aktivátorů. <sup>1</sup>H NMR analýza mikrostruktury polyhexenů rovněž ukázala, že volbou aktivátoru (kokatalyzátoru) lze ovlivňovat podíl CW reakce k propagaci a regulovat větvení polymeru a že všechny ne-MAO kokatalyzátory vedly k polyhexenu s nižším počtem větví, tj. umožňovaly vyšší rozsah CW reakce.

Další polymerace hex-1-enu pomocí ostatních Ni komplexů **3-9** byly prováděny pouze s nejaktivnějšími aktivátory DEAC a EADC a porovnávány s MAO s cílem posoudit živost polymerace. Dobře řízené polymerace vedoucí k polyhexenům s úzkou distribucí molární hmotnosti bylo dosaženo pouze u komplexů s nejobjemnějšími substituenty, tj. komplexy **3** a **5**. V případě použití methyl substituovaných komplexů **7** a **8** aktivovaných DEAC nebo EADC vznikaly polyhexeny s výrazně rozšířenou distribucí molární hmotností (Đ~2-3). Komplex **5**, který ve studii [**P3**] vykazoval při aktivaci MAO nejvyšší úroveň řízení, při aktivaci DEAC a EADC poskytoval polyhexen s disperzitou 1.3-1.4. To ukazuje, že živost polymerací iniciovaných komplexy s méně objemnými ortho arylovými substituenty diiminových ligandů je výrazně ovlivněna i volbou kokatalyzátoru. Živost polymerací je tak u těchto komplexů podmíněna využitím objemného kokatalyzátoru MAO, který pak v roli protianiontu kationtového růstového centra pravděpodobně pomáhá stéricky bránit přenosovým reakcím.

Pro polymerace hex-1-enu vedoucí k polyhexenu s nejnižší disperzitou, tj. polymerace aktivované DEAC a EADC a iniciované komplexem **3**, byly pro ověření živosti polymerace provedeny reiniciační testy. Překvapivě kombinace **1**/DEAC neprokázala živost polymerace, jak se ukázalo z významného rozšíření distribuce molárních hmotností vzorků odebraných z reakční směsi před přídavkem druhé dávky monomeru a na konci polymerace. Naopak sytém **1**/EADC vedl k dobře řízené polymeraci a bylo pomocí něj dosaženo zdvojnásobení molární hmotnosti polyhexenu při zachování její úzké distribuce po dobu celého experimentu. Jako vysvětlení byla navržena silnější koordinace DEAC na Ni centrum po spotřebování prvního podílu monomeru a jeho obtížnější náhrada monomerem po opětovném přidání hex-1-enu.

U komplexu **5** aktivovaného MAO, DAEC a EADC byla provedena kinetická studie, která potvrdila i vizuálně (změna barvy z oranžové na sytě fialovou) pozorovatelnou pomalejší aktivaci pomocí EADC. Pro systém **5**/EADC je tak z kinetických záznamů zřetelná indukční perioda na rozdíl od systémů **5**/MAO a **5**/DEAC, kde polymerace hex-1-enu sleduje hned od počátku kinetiku prvního řádu k monomeru. Při vynesení hodnot počátečních propagačních rychlostí v závislosti na koncentraci hlinitých aktivátorů je vidět, že tato závislost nejprve narůstá a při určité koncentraci [AI] dosahuje plata. Tento bod určuje minimální poměr aktivátoru k Ni komplexu nutný pro jeho účinnou aktivaci. Na rozdíl od MAO, pro které je tato hodnota Al/Ni rovna 50, dosahují DEAC a EADC ustálených hodnoty aktivit již od hodnot Al/Ni=5, což ukazuje na jejich výbornou aktivační schopnost.

V práci [P4] jsme rovněž studovali mechanismus aktivace pomocí UV-VIS spektroskopie. V předchozí studii<sup>28</sup> byla pro systém 5/MAO získána absorpční spektra obsahující signály s maximem kolem 530 a 700 nm a stabilita spektra byla korelována s živostí polymerace hex-1-enu. Při nízkých teplotách bylo spektrum neměnné, zatímco při zvýšení teploty, kdy dochází k nárůstu vedlejších reakcí, narůstala intenzita pásu při 700 nm a klesala intenzita pásu při 530 nm. Na základě toho byla navržena interpretace přiřazující pás při 530 nm aktivním polymeračním centrům a pás při 700 nm neaktivním částicím s neznámou strukturou. V našich experimentech však byl při aktivaci komplexu pomocí DEAC a EADC pozorován pouze vznik jednoho absorpčního pásu 530 nm. To by naznačovalo, že komplex 5 je pomocí těchto kokatalyzátorů kvantitativně převeden na katalytická centra. U systému 5/DEAC byl při polymeraci hex-1-enu pozorován zánik pásu při 530 nm asi po 8 h experimentu a zároveň byl pozorován vznik pásu při 650 nm a reakční směs změnila barvu z fialové na zelenou. V tomto okamžiku, kdy se dala očekávat již vysoká konverze monomeru, jsme přidali čerstvý hex-1-en. Překvapivě celá směs okamžitě změnila barvu na červenou a v UV spektru téměř zcela vymizel pás při 650 nm a znovu se objevil pás při 530 nm. Dalšími pokusy, při kterých byl komplex 5 aktivován pomocí DEAC v nepřítomnosti monomeru jsme ověřili, že opět vzniká pás při 650 nm a po přídavku monomeru se ve spektru okamžitě objevuje pás při 530 nm. Na základě provedených experimentů jsme navrhli, že pás

při 530 nm náleží struktuře aktivního alkyl-olefinového Ni komplexu (A) a pás při 650 nm alkyl-Ni komplexu B, ve kterém již není koordinován monomer a na jeho vazebném místě je molekula rozpouštědla nebo kokatalyzátoru, které lze přídavkem olefinu vytěsnit a regenerovat tak aktivní růstové centrum. Stejné vysvětlení však nelze aplikovat na MAO aktivované polymerace, kde se pík při 700 nm (B) vyskytuje již od začátku polymerace a další přídavek monomeru jeho intenzitu nemění. Terminačními experimenty se sloučeninami, které se vážou k Ni centru silněji než hex-1-en (např. styren či akrylát) bylo potvrzeno, že i struktura komplexu absorbujícího při 700 nm odpovídá komplexu, který obsahuje labilní ligand schopný substituce. Lze předpokládat, že část orbitalů Ni centra interaguje s objemným MAO kokatalyzátorem a neumožnuje tak plnou aktivaci všech Ni center. Silnější elektrondonor je však schopen tuto interakci přerušit a koordinovat se k centrálnímu kovu, což ukazuje, že se jedná o strukturu analogickou komplexu B.

#### Řízení morfologie polyolefinů připravených pomocí diiminových komplexů Ni [P5, P6]

V pracích [**P5**] a [**P6**] jsme ve spolupráci s prof. Cramailem (Univerzita Bordeaux) studovali možnosti řízení morfologie polyolefinů pomocí micelárních katalyzátorů na bázi α-diiminových komplexů Ni. Morfologie připravovaných polymerů je důležitá z hlediska stability provozu reaktoru (aby nedošlo k jeho "zapolymerování") a také z hlediska zpracování polymeru, kdy je výhodné, pokud je produkt reakce získán již ve formě granulátu. Pro řízení morfologie se většinou využívají heterogenní katalytické systémy vznikající imobilizací katalyzátorů na inertní nosič. Tím bývá silika nebo chlorid hořečnatý. Morfologie nosiče se pak často replikuje v morfologii vznikajícího polymeru.

V našem případě jsme využili pro přípravu polymerů s řízenou morfologií proces samouspořádávání koncově funkcionalizovaných polymerů, které v nepolárním prostředí (typicky využívaném pro koordinační polymerace olefinů) reagují s MAO a vytváří micely s polárním jádrem. Do těchto micel poté proniká i katalyzátor a vytváří s MAO katalyticky aktivní růstová centra. Polymerace se tak uskutečňuje v prostředí micely a vznikají částice polymeru, které replikují kulovitou symetrii micely (Obr. 4).

Tento postup byl poprvé využit pro přípravu milimetrových částic polyethylenů v micelách tvořených polystyrenovými řetězci končenými polárními skupinami benzoové kyseliny nebo benzofenonu nebo blokovými kopolymery styrenu. Jako katalyzátory byly použity bisiminopyridylové komplexy železa<sup>30, 31</sup>.



Obr. 4 Mechanismus tvorby micelárních katalytických systémů

V práci [P5] jsme pro tvorbu micel využili polyisoprenů připravených pomocí živé aniontové polymerace a končených polární difenylmethylolovou skupinou o molární hmotnosti 2500 g/mol. Tento polyisopren je schopen sám o sobě při koncentraci 1 mg/ml v heptanu vytvářet micely o hydrodynamickém poloměru 280 nm. Přídavek MAO nebo trimethylaluminia (TMA) vede k nárůstu velikost micel na 530-550 nm v důsledku enkapsulace organokovů v jádru micely. Bez přítomnosti polyisoprenových micel je MAO s heptanem nemísitelný a ihned po přídavku do heptanu se sráží. V přítomnosti micel je MAO zcela homogenně rozptýleno, což ukazuje na jeho přítomnost pouze v jádrech micel. Jako katalyzátory byly v této práci testovány bis(imino)pyridylový Fe komplex, bis(indenyl)ZrCl<sub>2</sub> a diiminového Ni komplexu 9 (viz. obr. 3). Fe a Zr katalyzátory produkují čistě lineární polyethylen, Ni komplex podléhající CW mechanismu poskytuje větvený PE. Méně objemné substituenty komplexu 9 byly voleny s ohledem na potlačení rozsahu CW reakce s cílem tvorby méně větveného PE. Fe komplex aktivovaný TMA vedl k tvorbě kulovitých PE částic s průměrem 1-10 µm, přičemž polymerace s vyšší katalytickou aktivitou poskytovaly menší PE částice. Zirkonocen poskytoval nehledě na podmínky syntézy pouze PE částice s průměrem kolem 1 μm. Překvapivě největší kulovité částice s rozměry 5-80 μm (Obr.4) poskytl Ni komplex 9 při 30°C aktivovaný MAO, kdy vznikal téměř amorfní PE (obsah krystalické fáze <1%) s teplotou tání kolem 60°C. Kinetickými měřeními bylo ověřeno, že přítomnost polyisoprenu v reakční násadě neovlivňuje kinetiku polymerace ethylenu, to je dáno zejména tím, že Al kokatalyzátor byl v přebytku v řádu desítek oproti hydroxy skupinám polyisoprenu.

V navazující práci [**P6**] jsme se pokusili nahradit složitě laboratorně syntetizovaný polyisopren komerčně dostupným polymerem. Jako jeden z nejběžněji dostupných nízkomolekulárních koncově funkcionalizovaných polymerů byl zvolen hydroxy terminový cis-1,4-polybutadien (PBD-OH) (Sartomer, Kralupy n. Vltavou, M<sub>n</sub>=4600 g/mol, Đ=1.05) připravovaný aniontovou polymerací pomocí

Li iniciátorů. Při prvotních testech schopnosti vytvářet micely v heptanu se ukázalo, že samotný PBD-OH v heptanu s MAO se micel nevytváří, což indikuje okamžité srážení MAO. Proto jsme se rozhodli koncovou skupinu transformovat na karboxylovou funkci, o které v případě polystyrenu bylo známo, že napomáhá samouspořádávání<sup>30</sup>. Z testovaných činidel se ukázaly nejlepší maleinanhydrid (vedoucí k PBD-MA) a trimesoyl chlorid (vedoucí po hydrolýze k 3,5-dikarboxyfenylovým skupinám; PBD-TRIMA) použité v 3 a 20 násobném nadbytku pro posunutí rovnováhy reakce a pro zamezení tvorby dimerů. Modifikované polybutadieny obsahovaly 3-10% dimerních molekul. Při koncentraci 1 mg/ml bylo pomocí DLS zjištěno, že samotné modifikované polybutadieny se nesamouspořádávají, ale přídavek MAO vede v obou případech k tvorbě sférických částic s průměrem 40-100 nm, které stabilizují MAO roztok. V případě použití TMA tvořil dobře definované kulovité částice o velikost kolem 90 nm pouze molekuly PBD-TRIMA, PBD-MA vytvářel s TMA méně definované částice s nekulovitou symetrií.

Micelární nosičové systémy byly dále testovány při homopolymeracích ethylenu a oktadec-1enu katalyzovaných diiminovými komplexy niklu. Pro polymerace ethylenu byl volen komplex **7** (Obr.3), který díky svým malým methylovým ortho-arylovým substituentům potlačuje CW a umožňuje přípravu semikrystalického PE. Pro polymerace oktadec-1-enu jsme naopak vybrali katalyzátory **3** a **5** (Obr.3), které by rozsáhlým CW přenosem poskytovaly polyoktadecen s vysokým podílem 1,18- a 2,18zapojení monomeru vedoucí opět k semikrystalickému polymeru připomínajícímu svou strukturou lineární PE. Pro srovnání byl využit také bis(indenyl)ZrCl<sub>2</sub>.

Pro další potlačení rozsahu CW reakce byla volena teplota polymerace ethylenu 0°C. Oba nosičové systémy PBD-MA a PBD-TRIMA použité v koncentracích 0.5-2 mg/ml poskytly pomocí **7**/MAO PE částice se srovnatelnou morfologií a velikostí částic okolo 5 µm. Polymerace bez přítomnosti PBD nosiče vedle k částečně řízené morfologii, kdy PE částečky jsou spojeny vlákny a vytváří větší aglomeráty. V případě PBD-MA bylo možno koncentrací nosiče řídit molární hmotnost vznikajícího PE. Vyšší koncentrace micel vedla k nižší molární hmotnosti, což odpovídá předpokladu, že polymerace probíhá pouze v micelách. Za zmínku stojí i fakt, že použití nosičů rovněž zvýšilo o 5-10°C teploty tání připravených PE, což souvisí s ovlivněním podílu propagační a CW reakce ve prospěch propagace. Při použití TMA jako kokatalyzátoru a PBD-MA byly získány PE částice s podobnou morfologií jako v nepřítomnosti nosiče. To souvisí se špatnou tvorbou micel PBD-MA pomocí TMA jak vyplývá z DLS měření.

Při polymeracích ethylenu pomocí bis(indenyl)ZrCl<sub>2</sub>/MAO v přítomnosti PBD-MA nosiče došlo k asi 10x nižšímu poklesu aktivity než při použití blokových kopolymerů polyisopren-blok-polymethylmethakrylát (PI-b-PMMA). Důvodem je výrazně nižší obsah kyslíkových atomů v PBD-MA ve srovnání s PI-b-PMMA jehož esterové skupiny snadno deaktivují zirkonocenový katalyzátor.

S cílem dosáhnout živé polymerace zároveň vedoucí k částicím s řízenou morfologií jsme se pokusili o polymeraci otadec-1-enu pomocí Ni diiminových komplexů **3** a **5** a v přítomnosti PBD-MA a PBD-TRIMA. Diiminové Ni katalyzátory totiž živou polymeraci umožňují pouze v případě vyšších olefinů, nikoliv ethylenu. Zároveň volba monomeru při významném CW přeuspořádání řetězce povede k dlouhým lineárním úsekům připomínajícím strukturu lineárního PE a umožní krystalizaci takového polymeru. Ke srážení částic polyoktadecenu docházelo pouze při použití komplexu **5** vykazujícím nejvyšší míru CW procesu. Morfologie připravených polyoktadecenů pomocí micelárních systémů se však výrazně neodlišovala od nenosičového systému a nebylo tedy dosaženo pravidelných kulovitých částic.

Z uvedených experimentů, ve kterých jsme se snažili připravovat spíše semikrystalické polymery, které by se dobře srážely z reakční směsi, vyplývá, že pro tvorbu větších částic pomocí micelárních systémů je naopak výhodnější spíše tvorba amorfního polymeru.

### 2.2 Polymerace ethylenu a styrenu pomocí metalocenových komplexů

### Polymerace ethylenu pomocí titanocenů a zirkonocenů nesoucích objemné Cp ligandy [P7]

Substituce cyklopentadienylových kruhů má zásadní vliv na aktivitu metalocenových komplexů i na molární hmotnost jimi poskytovaných polymerů. Relativně málo studovanou skupinou metalocenů jsou komplexy nesoucí cyklopentadienylové ligandy substituované fenylovými skupinami. V práci [P7] byly pro polymeraci ethylenu testovány Zr a Ti komplexy nesoucí jeden nebo dva 1,4-dimethyl-2,3difenyl-cyclopentadienylové ligandy připravené dr. Jiřím Pinkasem (ÚFCH JH AV ČR). Katalytické chování nově připravených sloučenin bylo porovnáváno se základním zirkonocenem  $\{\eta^{5}-(C_{5}H_{5})\}_{2}$ ZrCl<sub>2</sub>. Komplexy byly aktivovány methylalumoxanem (900 ekv. k Zr). Polymerace probíhaly v toluenu za atmosférického tlaku. Komplexy { $\eta^{5}$ -(1,4-Me<sub>2</sub>-2,3-Ph<sub>2</sub>C<sub>5</sub>H)}<sub>2</sub>ZrCl<sub>2</sub> a { $\eta^{5}$ -(1,4-Me<sub>2</sub>-2,3-Ph<sub>2</sub>C<sub>5</sub>H) }{ $\eta^{5}$ - $(C_5H_5)$ /ZrCl<sub>2</sub> nesoucí jeden nebo dva vysoce objemné substituenty byly na rozdíl od standardu { $\eta^5$ -(C5H5)2}ZrCl2 při 30-50°C téměř neaktivní. Při 80°C došlo k výraznému nárůstu aktivity na zhruba 50% hodnot dosahovaných pro  $\{\eta^{5}-(C_{5}H_{5})_{2}\}$ ZrCl<sub>2</sub>. To ukazuje, že při studiu polymeračního chování katalyzátorů je potřeba zkoumat širší interval reakčních podmínek tak, aby nebyly nové sloučeniny odsouzeny jako polymeračně neaktivní. U komplexu  $\{\eta^{5}-(1,4-Me_{2}-2,3-Ph_{2}C_{5}H)\}_{2}$ ZrCl<sub>2</sub> byl studován vliv poměru MAO/Zr, jehož snižování z 900 na 200 vedlo rovněž ke snížení aktivity o 2 řády, což je v souladu s obecným chováním metalocenů, pro jejichž aktivaci se používá MAO v poměru stovek až 10 000. Nižší aktivita komplexů fenyl substituovanými Cp ligandy může být také způsobena elektronakceptorním vlivem Ph skupin, která může vést k destabilizaci kationtových růstových center a tedy jejich nižší koncentraci. Molární hmotnosti připravených polyethylenů jsou blízké těm připraveným pomocí { $\eta^{5}$ - ( $C_{5}H_{5}$ )<sub>2</sub>}ZrCl<sub>2</sub> naznačující podobný poměr mezi rychlostmi propagačních a přenosových reakcí. Všechny připravené polyethyleny jsou vysoce lineární, jak ukazují jejich teploty tání kolem 130°C. Na rozdíl od obou zirkonocenů byl titanocenový katalyzátor { $\eta^{5}$ -(1,4-Me<sub>2</sub>-2,3-Ph<sub>2</sub>C<sub>5</sub>H)}<sub>2</sub>TiCl<sub>2</sub> téměř zcela neaktivní při všech testovaných teplotách (30-80°C). Stejné chování bylo již dříve pozorováno pro podobný titanocen { $\eta^{5}$ -(1,4-Ph<sub>2</sub>-2,3-Me<sub>2</sub>C<sub>5</sub>H)}<sub>2</sub>TiCl<sub>2</sub>/MAO <sup>32</sup>. Vysvětlením pro neaktivitu titanocenů je přeměna aktivních Ti kationtových center na neaktivní Ti<sup>3+</sup> centra redukcí pomocí MAO nebo trimethylaluminia, které je v MAO vždy přítomno.

#### Polymerace a kopolymerace ethylenu pomocí titanocenů s ligandy na bázi kafru [P8]

Pro aktivaci metalocenových komplexů je důležitý i charakter  $\sigma$ -ligandů vázaných na centrální kov. Těmi nejčastěji bývají halogenidové nebo alkoxy skupiny. Snadnost s jakou lze provádět jejich substituci a abstrakci pomocí organohlinitého kokatalyzátoru ovlivňuje rychlost tvorby růstových center a také určuje nezbytné množství (nadbytek) Al kokatalyzátoru<sup>33</sup>. V práci [P8] jsme se zabývali zkoumáním katalytické aktivity nových dicyklopentadienylových komplexů titanu nesoucích σ-ligandy (L) odvozené od hydroxyderivátů kafru (Obr. 5) připravených v laboratoři prof. Carvalho (Instituto Superior Técnico). Kafrové substituenty jsou na centrální atom Ti vázány po deprotonaci (Et<sub>3</sub>N) přes kyslíkové atomy, případně i přes dusíkový atom oximové skupiny v případě ligandu <sup>2</sup>LH (bidentátní ligand). Komplexy s obecnou strukturou (Cp<sub>2</sub>LTiCl) byl aktivovány přebytkem MAO a jejich aktivita byla porovnána s Cp<sub>2</sub>TiCl<sub>2</sub> jako standardem. Všechny komplexy byly srovnány z hlediska jejich polymerační aktivity při 50°C a Al/Ti=1000 v toluenu při tlaku ethylenu 0.1 MPa. Komplex Cp<sub>2</sub><sup>3</sup>LHTiCl byl zcela neaktivní, což bylo způsobeno jeho velmi malou rozpustností v toluenu a to i po aktivaci MAO. Komplex Cp<sub>2</sub><sup>1</sup>LTiCl měl za stejných podmínek polymerační aktivitu blízkou standardu Cp<sub>2</sub>TiCl<sub>2</sub>, přičemž komplex Cp<sub>2</sub><sup>2</sup>LTiCl byl asi o 20% více aktivní než Cp<sub>2</sub>TiCl<sub>2</sub>. Při prodloužení reakční doby se rovněž ukázalo, že aktivita katalyzátoru Cp<sub>2</sub><sup>2</sup>LTiCl s časem klesá, zatímco aktivita Cp<sub>2</sub><sup>1</sup>LTiCl během 1h mírně roste. Molární hmotnosti PE získaných pomocí Cp2<sup>1</sup>LTiCl a Cp2<sup>2</sup>LTiCl jsou téměř dvojnásobné oproti těm získaným pomocí Cp<sub>2</sub>TiCl<sub>2</sub>, což ukazuje na nižší počet růstových center vytvořených v případě komplexů Cp<sub>2</sub><sup>1</sup>LTiCl a Cp<sub>2</sub><sup>2</sup>LTiCl v důsledku obtížnější abstrakce kafrových ligandů z centrálního atomu Ti. Přes rozdílné hodnoty molárních hmotností PE získaných pomocí všech tří komplexů je distribuce molárních hmotností těchto PE prakticky identická (plyne z SEC), což ukazuje, že ve všech případech vzniká reakcí komplexů s MAO stejné růstové centrum (Cp₂TiMe<sup>+</sup>). Přes asi 20% rozdíl v aktivitách komplexů Cp<sub>2</sub><sup>1</sup>LTiCl a Cp<sub>2</sub><sup>2</sup>LTiCl jsou molární hmotnosti získaných PE prakticky shodné, což ukazuje, že molární hmotnost PE je dána zejména poměrem přenosových reakcí k propagaci. Dle očekávání komplexy poskytly lineární PE s teplotou tání asi 140°C. Dále bylo zjištěno, že komplexy Cp<sub>2</sub><sup>1</sup>LTiCl a Cp<sub>2</sub><sup>2</sup>LTiCl jsou zcela neaktivní při polymeraci hex-1-enu, ale dokáží efektivně kopolymerovat ethylen s norbornenem.

Tyto kopolymery představují speciální materiály (COC-cyclic olefin copolymers, např. TOPAS), které mají vysokou T<sub>g</sub>=150-200°C a vyznačují se vysokou transparentností. Rychlost kopolymerace ethylenu s norbornenem pomocí komplexů Cp<sub>2</sub><sup>1</sup>LTiCl a Cp<sub>2</sub><sup>2</sup>LTiCl byla oproti homopolymeraci ethylenu asi poloviční v důsledku vyšší sterické náročnosti norbornenu. Komplex Cp<sub>2</sub><sup>2</sup>LTiCl byl opět aktivnější než komplex Cp<sub>2</sub><sup>1</sup>LTiCl. Monomodální SEC křivky naznačují vznik kopolymerů. Disperzita kopolymerů je nižší než v případě homopolymeru ethylenu, což je způsobeno homogenním charakterem kopolymerace, kdy vznikající kopolymer je rozpustný v polymeračním prostředí. Pomocí kvantitativní <sup>13</sup>C NMR spektroskopie byl stanoven obsah norbornenových jednotek 13-14 mol%, což odpovídá T<sub>g</sub> kolem 10°C. Dle NMR spekter se norbornen podle očekávání zapojoval do hlavního řetězce adicí dvojné vazby. Minoritní signály NENEN a EENEE v NMR spektrech naznačují izolované nebo alternující norbornenové jednotky spíše než delší sekvence tvořící bloky norbornenu. Jeden z připravených kopolymerů vykázal i teplotu tání kolem 180°C, což je rovněž v souladu s termickým chováním alternujících kopolymerů ethylenu a norbornenu<sup>34</sup>.



Obr. 5 Struktura kafrových derivátů využitých jako σ-ligandy titanocenových komplexů Cp<sub>2</sub>LTiCl

#### Syndiospecifická polymerace styrenu pomocí polometalocenových komplexů titanu [P9-P10]

V pracích [**P9**]-[**P10**] jsme se zabývali studiem polymeračního chování monocyklopentadienylových Ti komplexů při polymeraci styrenu poskytující syndiotaktický polystyren. Testované komplexy byly připraveny v laboratoři doc. Milana Erbena (Univerzita Pardubice).

Úvodní krok katalytického cyklu polymerace olefinů vždy zahrnuje koordinaci elektronově bohatého olefinu na elektronově chudé kovové centrum. Při snížení elektronové hustoty na kovovém centru substitucí ligandů pomocí elektronakceptorních substituentů tak lze očekávat nárůst polymerační aktivity. V práci [**P9**] byla proto zkoumána řada nových titanocenových komplexů s Cp ligandy substituovanými chloro- a fluoroalkylsilylovými skupinami (Obr. 6) s rozdílnými elektronovými efekty a byl sledován vliv této substituce na polymeračních chování Ti komplexů. Pomocí NMR a UV- VIS spekter bylo stanoveno, že elektronakceptorní efekt mají pouze trihalosilylové substituenty v komplexech **3** a **6**. Vliv monohalo(dimethyl)silylových a dihalo(monomethyl)silylových skupiny byl vyhodnocen jako elektrondonorní. Poslední v sérii byl analog komplexu 4 komplex CpSiMe<sub>2</sub>FTiF<sub>3</sub> 7, u kterého byly chlorové ligandy Ti centra nahrazeny fluorovými. U komplexu 7 byla zjištěna v pevné fázi tvorba pentamerních agregátů. Komplexy 1-7 a komplex CpTiCl<sub>3</sub> jako standard byly po aktivaci přebytkem MAO testovány při polymeraci styrenu. Komplexy 1-6/MAO vykázaly srovnatelné polymerační aktivity jako CpTiCl<sub>3</sub>/MAO standard. Oproti očekávání se výrazně neprojevil elektronový vliv substituentů, což může být způsobeno poměrně dlouho polymerační dobou, při které ve všech případech styren dosáhl již vysoké konverze. Všechny připravené polystyreny byly syndiotaktické jak vyplývá v rozmezí 250-265°C. Polystyreny z jejich teplot tání připravené pomocí halosilylsubstituovaných komplexů 1-6 byly výrazně více syndiotaktické než polystyren získaný pomocí CpTiCl<sub>3</sub> jak vyplývá z jejich teplot tání vyšších o více než 10°C. Zavedení halosilylových substituentů na cyklopentadienylové kruhy vedlo k výraznému zvýšení molární hmotnosti připravených polystyrenů oproti CpTiCl<sub>3</sub>. Pravděpodobným důvodem je zvýšení sterických zábran u substituovaných ligandů a v jejich důsledku potlačení přenosových reakcí. Sterické stínění center také mohlo být zvýšeno interakcemi objemných MAO molekul s halogenovými atomy v silylových skupinách. Všechny připravené polystyreny měly úzkou distribuci molárních hmotností, což potvrzuje jednotný charakter růstových center v homogenním katalytickém systému (single-site). Komplex 13 měl ze všech zkoumaných komplexů nejnižší aktivitu, což je způsobeno jeho oligomerní strukturou. Navýšení aktivity nebylo u komplexu 13 dosaženo ani několikanásobným zvýšením množství použitého kokatalyzátoru MAO jak bylo pozorováno u mateřského systému CpTiF<sub>3</sub>/MAO<sup>35</sup>. Vliv elektronových efektů substituentů ve studovaných komplexech na katalytickou aktivitou tedy nebyl pozorován.

Obr. 6 Struktura halosilyl substituovaných Ti komplexů 1-7

V další práci [**P10**] byla testována série nových monocyklopentadienylových komplexů titanu substituovaných na Cp cyklech alkoxysilylovými skupinami. Dalšími ligandy přímo vázanými na Ti atom byly alkoxyskupiny (MeO-, iPrO-, tBuO-) (Obr. 7). Pro srovnání byl použit komplex CpTiOMe<sub>3</sub> a dále byly připraveny trimethylsilyl substituované komplexy CpSiMe<sub>3</sub>Ti(OR)<sub>3</sub> (R=Me, iPr, tBu). Všechny

komplexy byly pro polymeraci styrenu aktivovány MAO a poskytly jako produkt vysoce syndiotaktický polystyren s teplotou tání 260-270°C. Nejaktivnější byly komplexy CpTi(OMe)<sub>3</sub>, CpSiMe<sub>3</sub>Ti(OMe)<sub>3</sub> a CpSiMe<sub>3</sub>Ti(OtBu)<sub>3</sub>. Alkoxysubstituované deriváty 8-11 vykázaly 5-10 x nižší aktivitu. Jako vysvětlení byla navržena koordinace MAO ke kyslíkovým atomům alkoxysilyl skupin, která vedla k výraznému zvýšení sterické zábrany Cp ligandu a omezení aktivity komplexů. Intramolekulární koordinaci O atomů alkoxysilylových skupin k Ti centru lze vzhledem k prostorové struktuře komplexů vyloučit. Intermolekulární interakce kyslíkových atomů k Ti centrům je málo pravděpodobná vzhledem k nízkým koncentracím Ti katalyzátorů. Syndiotakticita připravených polystyrenů byla vedle teplot tání stanovována i pomocí kvantitativní <sup>13</sup>C NMR spektroskopie. S výjimkou polystyrenu připraveného pomocí CpTiOMe<sub>3</sub> všechny ostatní připravené polystyreny vykazovaly pouze jeden signál odpovídající rrrrr hexadám nebo rrrrrrr heptádám a synditakticita tak byla vyšší než 99%. Pouze u polystyrenu připraveného pomocí základního derivátu CpTiOMe₃ byl v NMR spektru pozorován signál meso defektů a obsah syndiotaktických heptád byl 97.6 %. Alkoxysubstituované komplexy tedy vedou k vysoce syndiospecifickým polystyrenům ovšem jejich polymerační aktivita je podstatně nižší ve srovnání s trimethylsilyl substituovanými komplexy, které poskytují srovnatelně stereoregulární polystyren při zachování vysoké aktivity.



Obr. 7 Struktura alkoxysilyl substituovaných komplexů 8-11

## 3. Závěr

Habilitační práce shrnuje výsledky naší laboratoře v oblasti katalytických polymerací olefinů. Hlavní výzkumná pozornost byla zaměřena na polymerace olefinu katalyzované homogenními katalytickými systémy, zejména diiminovými komplexy niklu a paladia, ale i metalocenovými komplexy na bázi zirkonia a titanu připravenými ve spolupracujících laboratořích.

Za zásadními výsledky považuji:

- a) Prostudování vlivu struktury diiminových ligandů Ni komplexů na živost polymerace olefinů, kdy byla výrazně rozšířena knihovna komplexů schopných živé polymerace, s tím souvisí i rozšíření možností řízení větvení vznikajících polymerů volbou struktury komplexu
- b) Zmapování reakčních podmínek, ze kterých je možno provádět živé polymerace pomocí diiminových komplexů niklu, zejména možnosti přípravy polymerů s úzkou distribucí i za laboratorní teploty a v širokém rozpětí poměrů monomer/iniciátor, které umožňuje přípravu polymerů s definovanou molární hmotností v rozsahu 10<sup>3</sup>-10<sup>5</sup> g/mol
- c) Prostudování mechanismu aktivace diiminových Ni komplexů a navržení nové interpretace absorpčních spekter založené na konkrétních strukturách Ni komplexů
- d) Nalezení nových katalytických systémů využívajících pro aktivaci Ni diiminových komplexů jednoduchých organohlinitých sloučenin
- e) Prostudování kinetiky polymerací olefinů katalyzovaných Ni diiminovými komplexy, které vedlo i k objevení isomerace monomeru pomocí katalyzátorů s méně stericky objemnými substituenty.
- f) Přípravu polyethylenových částic s kulovitou morfologií pomocí micelárních nosičových systému na bázi diiminových komplexů niklu
- g) Prozkoumání vlivu struktury titanocenů nesoucích na Cp ligandech halosilylové nebo alkoxysilylové skupiny na jejich katalytické chování při syndiospecifické polymeraci styrenu

Výšeuvedené poznatky byly cenným zdrojem "know-how" při přípravě modelových polymerů připravovaných pomocí diiminových komplexů niklu a paladia v rámci aktuálně probíhajících projektů.

Součástí výzkumné činnosti bylo i vybavení laboratoře aparaturami pro syntézy katalyzátorů a provádění tlakových polymerací olefinů ve vysoce inertních podmínkách, zároveň byly díky novému instrumentálnímu vybavení zavedeny pokročilé metody charakterizace připravovaných polymerů.

# 4. Použité symboly a zkratky

| tBu       | terc. butyl   |
|-----------|---|
| COC       | cyclic olefin copolymer   |
| Ср        | cyklopentadienyl  |
| CW        | chain walking   |
| DLS       | dynamický rozptyl světla  |
| MAO       | methylaluminoxan  |
| Me        | methyl  |
| iPr       | isopropyl   |
| PBD-OH    | hydroxy terminovaný cis-1,4-polybutadien                        |
| PBD-MA    | PBD-OH esterifikovaný maleinyhydridem                           |
| PBD-TRIMA | PBD-OH esterifikovaný trimesoyl chloridem a hydrolyzovaný vodou |
| PE        | polyethylen   |
| TMA       | trimethylaluminium  |
| Tg        | teplota skelného přechodu                                       |

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**P1** 

# Polymerization of hex-1-ene initiated by diimine complexes of nickel and palladium

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#### Abstract

The effect of monomer concentration, reaction temperature and initiator structure on the activity, molar mass, branching and thermal properties of poly(hex-1-ene)s was investigated for the polymerization of hex-1-ene initiated by four  $\alpha$ -dimine complexes of nickel and palladium. Hex-1-ene polymerization exhibits an apparent negative kinetic order with respect to monomer concentration. Polymerization of hex-1-ene initiated by MAO activated 1,4-bis(2, 6-diisopropylphenyl)acenaphtenediiminenickel(II) dibromide (**1a**/MAO) proceeds in living-like fashion not only at sub-zero temperatures but even at 20 °C. However, molar masses of the polymers are higher than predicted values in agreement with an initiator efficiency lower than one.

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#### 1. Introduction

Until recently, late transition metal complexes (especially nickel derivatives) were mainly known as oligomerization catalysts for olefins and some of them have found important applications in industry (Shell Higher Olefin Process) [1]. This is only in 1995 that Brookhart has reported the possibility to use nickel and palladium complexes with bidentate diimine ligands for the production of high molar mass polyolefins [2]. Bulky aromatic substituents on ligands which hinder axial positions of metal centers, avoid transfer reactions and play a key role for the polymerization ability of these catalysts. The proper choice of ligands allowed the design of nickel catalysts extremely resistant to chain transfer processes and capable to polymerize olefins in a living-like fashion [3–5]. A specific character of these catalytic systems is their ability to yield chain-end isomerization during the polymerization reaction. This results from the so-called chain walking mechanism in which the active catalytic site can migrate all along the last inserted monomer unit before a new monomer insertion takes place at the new metal center position. As a consequence, the resulting polyolefins exhibit a

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specific chain structure characterized by relatively ill-defined monomer units and branching. Detailed studies on the structure and the proportion of different types of branches, according to the olefin and to the reaction conditions, have been reported [6–10]. Indeed, a vast majority of these studies were performed with market leader ethylene and propylene monomers while higher  $\alpha$ -olefins were the subject of more limited investigations. Besides, only few studies have been concerned with the influence of the chain-end isomerization process onto the kinetic aspects of these polymerizations. An apparently negative order of the polymerization with respect to monomer was noticed but correlation with the chain walking mechanism is still controversial [11–14].

Here, we report a new study of hex-1-ene polymerization initiated by nickel and palladium diimine complexes. The effect of complex structure and reaction conditions, in particular the influence of monomer concentration, on polymerization activity and poly(hex-1ene) properties is investigated and discussed.

#### 2. Experimental part

All manipulations with air-sensitive compounds were done using standard Schlenk or high-vacuum line techniques. Nitrogen (SIAD, 99,999%) was purified by passing through column of Cu catalyst and molecular sieves to remove traces of oxygen and water.

Chlorobenzene (p.a., Penta) was refluxed over  $P_4O_{10}$ and distilled under nitrogen. Hex-1-ene (99%, Neraten 6, Spolana Neratovice) was dried over sodium and distilled under nitrogen. MAO (10 wt.% solution in toluene, Crompton) was used as such. Nickel and palladium derivatives were synthesized and purified according to literature procedures [3,15]. Palladium complexes were characterized by NMR. Purity of nickel initiators was proved by tests of polymerization activity which was found comparable with previously published results [3].

Polymerizations were carried out under dry nitrogen in chlorobenzene in a magnetically stirred 250 ml glass reactor. Polymerization procedure for Ni initiators consist of subsequent addition of chlorobenzene, hex-1-ene, initiator and activator. After desired reaction time polymerization was quenched by adding of 10 ml 10% HCl in MeOH, polymer was precipitated in 300 ml of MeOH and dried at room temperature until constant weight. In case of Pd complexes the polymerization was started by addition of initiator to hex-1-ene solution in chlorobenzene. Polymerization was quenched by pouring the reaction mixture into the tarred round bottom flask with 50 ml. Solution was dried until constant weight. For further characterization, catalyst from polymer was removed by dissolving in hexane and passing through the column with alumina and silica gel followed by precipitation in MeOH. Polymers were characterized as indicated below.

Some polymerization runs were repeated to check the reproducibility of results (e.g. Table 1, entry 5 and 15).

The structure of poly(hex-1-ene) chains was determined by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy. NMR spectra of polymers were recorded on Bruker Avance 300, 400 or 500 MHz spectrometers in CDCl<sub>3</sub> solution (20 w/v %) at 30 °C. The total number of branches per 1000 carbon atoms was determined by the integration of methyl signals with respect to signals of all protons in <sup>1</sup>H-NMR spectrum.

<sup>13</sup>C-NMR spectra of poly(hex-1-ene)s were carried out typically 6–8h using 70° pulse and relaxation delay of 4s to allow quantification [10]. Chemical shifts were referenced internally to the major backbone methylene carbon resonance, which was taken at 30.00 ppm from TMS. On labels *xBy*, *By* is a branch of length *y* carbons, *x* is the carbon being discussed, and the methyl at the end of the branch is numbered 1. Thus, the second carbon from the end of a butyl branch is 2B4. *xBy*+ refers to branches of length *y* and longer. When *x* in *xBy* is replaced by a br, the methine carbon of that branch is denoted.

Methylenes in the backbone are labeled with Greek letters which indicates how far from a branch point methine each methylene is. Greek letters with prime present methylenes between paired branches. The latter are labeled by 2 numbers 1, *m* where *m* is the number of carbons between two tertiary carbons, 1 being the closest tertiary carbon and m the other. Thus,  $\gamma$ B1+ refers to methylenes  $\gamma$  from a branch of length 1 or longer and 1,6- $\beta$ ' B1 are  $\beta$  methylenes between 1,6-paired methyl branches. A' and B' are the methyls of the methyl and ethyl branches, respectively, which comprise the *sec*-butyl ended branch (Scheme 1).

Molar masses were determined on Varian size exclusion chromatograph equipped with four TSK Gel G columns (2000 HXL, 5 $\mu$ m; 3000 HXL, 6 $\mu$ m; 4000 HXL, 6 $\mu$ m; 5000 HXL, 9 $\mu$ m) and RI detector at 25°C in THF solution (3mg/1ml THF) at an elution rate of 0.8 mlmin<sup>-1</sup> against PS standards <sup>1</sup>. DSC analyses were performed on a TA Instrument module Q100 using 10°C min<sup>-1</sup> heating rate.

<sup>&</sup>lt;sup>1</sup> Determination of poly(hex-1-ene) molar mass prepared with similar nickel initiator and exhibiting structure rearrangement between 0% and 60% was already performed by SEC-MALS [12]. A good correlation was found with poly(hex-1-ene) molar masses obtained by SEC-RI based on polystyrene calibration.

Table 1 Hex-1-ene polymerization using nickel and palladium complexes

| Entry          | Catalyst | $t_{\rm pol}$ | [HEX] <sup>a</sup> | T <sup>b</sup> | Activity <sup>c</sup>   | $Y_{\rm w}^{\rm d}$ | $M_n^{e}$              | P.I. <sup>f</sup> | T <sub>g</sub> <sup>g</sup> | $N^h$ |
|----------------|----------|---------------|--------------------|----------------|---|---------------------|------------------------|-------------------|-----------------------------|-------|
|                |          | (h)           | $(moll^{-1})$      | (°C)           | $(\text{kg}(\text{mol}_{\text{Ni}}\text{h}\text{mol}\text{l}^{-1})^{-1})$ | (%)                 | (kgmol <sup>-1</sup> ) |                   | (°C)                        |       |
| 1              | 1a       | 1             | 0.8                | 0              | 107   | 25.5                | 150                    | 1.15              | -53                         | 116   |
| 2              | 1b       | 1             | 0.8                | 0              | 28  | 6.8                 | 53                     | 1.11              | _                           | 89    |
| 3 <sup>i</sup> | 2a       | 5             | 0.8                | 40             | 3   | 3.9                 | 13                     | 5.21              | _                           | 74    |
| $4^{i}$        | 2b       | 5             | 0.8                | 40             | 12  | 13.1                | _                      | _                 | _                           | 79    |
| 1              | 1a       | 1             | 0.8                | 0              | 107   | 25.5                | 150                    | 1.15              | -53                         | 116   |
| 8              | 1a       | 2             | 0.8                | 0              | 103   | 47.0                | _                      | _                 | _                           | _     |
| 5              | 1a       | 1             | 0.8                | 20             | 201   | 49.0                | 268                    | 1.18              | _                           | 103   |
| 15             | 1a       | 1             | 0.8                | 20             | 205   | 47.1                | 278                    | 1.15              | _                           | _     |
| 6              | 1a       | 1             | 0.8                | 40             | 201   | 47.8                | 302                    | 1.42              | _                           | 99    |
| 9              | 1a       | 1.5           | 0.8                | 40             | 152   | 53.8                | _                      | _                 | _                           | _     |
| 7              | 1a       | 1             | 0.8                | 60             | 207   | 48.6                | 259                    | 1.38              | _                           | 98    |
| 10             | 1a       | 1             | 0.2                | 0              | 82  | 18.7                | 60                     | 1.07              | -56                         | 105   |
| 11             | 1a       | 1             | 0.4                | 0              | 104   | 25.4                | 95                     | 1.10              | _                           | 103   |
| 12             | 1a       | 1             | 1.8                | 0              | 80  | 18.7                | 262                    | 1.16              | _                           | 120   |
| 13             | 1a       | 1             | 2.8                | 0              | 72  | 17.2                | 331                    | 1.25              | _                           | 122   |
| 14             | 1a       | 1             | 5.8                | 0              | 47  | 10.6                | 434                    | 1.30              | -46                         | 135   |

Total volume of chlorobenzene and hex-1-ene 100 ml,  $[Ni] = 200 \,\mu mol l^{-1}$ ,  $[Al] = 5 \,mmol l^{-1}$ .

- Not determined.

<sup>a</sup> Initial concentration of hex-1-ene.

<sup>b</sup> Polymerization temperature.

<sup>c</sup> Activity: mass of polymer/(catalyst concentration\*monomer concentration\*polymerization time).

 $^{\rm d}$  Y<sub>w</sub> gravimetric conversion, mass of polymer/mass of monomer\*100.

<sup>e</sup> Molar mass determined by SEC against polystyrene standard.

<sup>f</sup> Polymolecularity index,  $M_{\rm w}/M_{\rm n}$ .

<sup>g</sup> Determined by DSC (heating rate  $10^{\circ}$ Cmin<sup>-1</sup>).

<sup>h</sup> Number of branches per 1000 carbon atoms determined by <sup>1</sup>H-NMR spectroscopy.

<sup>i</sup> [Pd] =  $200 \,\mu mol \, l^{-1}$ .



Scheme 1.

#### 3. Results and discussion

The mechanism of  $\alpha$ -olefin polymerization using palladium and nickel diimine complexes have been thoroughly studied by Brookhart and his coworkers [2,7,15]. In complement to these studies and with the aim to understand the influence of the chain walking mechanism on the kinetics of polymerization, hex-1ene polymerization in the presence of both palladium and nickel diimine complexes was investigated. The structures of the different metal complexes used as catalyst precursor are given in Fig. 1. Palladium complexes (2) were synthesized in the form of ionic salts. The cationic moiety already constitutes active specie and therefore no activator is required. Neutral dichloro complexes of nickel (1) have to be activated. This was achieved by adding methylalumoxane at a constant Al/Ni ratio of 250 which was shown to be optimal [11]. Polymerizations were performed in chlorobenzene at different temperatures ranging from 0 to  $60 \,^{\circ}$ C. The main results are summarized in Table 1.

Palladium catalysts are generally less active than nickel/MAO systems so the polymerization temperature was increased and reaction time, typically 1 h, prolonged



Fig. 1. Structures of nickel and palladium complexes.

to 5h. Nevertheless, the yields  $(Y_w)$  obtained with palladium complexes remained low.

A great influence of the diimine substituent structure is observed with both Ni and Pd complexes. Nickel derivative **1a** is approximately three times more active than complex **1b** (Table 1, entries 1 and 2). The opposite order of activity is observed for palladium complexes **2a** and **2b** bearing the same diimine ligands (Table 1, entries 3 and 4).

The effect of reaction temperature on activity was studied in the case of **1a/MAO**. Increasing the temperature from  $0^{\circ}$ C to  $20^{\circ}$ C yields a twofold activity increase but further temperature rise has no significant influence on activity (Table 1, entries 1, 5, 6, 7). This may be the result of the simultaneous increase of propagation rate and the opposite effect of active species deactivation.

Comparison of poly(hex-1-ene) molar masses obtained by nickel and palladium catalysts (Table 1, entries 1 and 3) shows that nickel catalysts produce polymers with significantly higher molar masses than the palladium one. Increase of initial monomer concentration from 0.2 M to 5.8 M regularly increases the polymer molar mass from 60 to 430 kg mol<sup>-1</sup> in case of Ni initiator 1a/MAO (Table 1, entries 1, 10-14). We tentatively plotted in Fig. 2 the experimental poly(hex-1-ene)s molar masses obtained at 0°C and 20°C versus theoretical ones, assuming one chain formed by initial **1a** complex. A linear relationship is observed suggesting that polymerization present some living-like character and in particular a propagation reaction without noticeable transfer and termination as well as a rapid initiation and the formation of an almost constant proportion of active species. Comparison of experimental molar masses with theoretical ones reveals that experimental values are significantly higher than predicted ones (Table 2) indicating that the initial complex is not completely activated. The initiation efficiency with respect to the initial nickel dichloride complex can be estimated to about 0.6. This is in agreement with previous results of Peruch et al. who carried out UV-VIS study of similar catalytic system [11].



Fig. 2. Comparison of experimental and theoretical number average molar mass of poly(hex-1-ene) prepared by Ni complex 1a/MAO at 0 °C in chlorobenzene, [HEX] = 0.2-5.8 M.

It was already shown that olefin polymerization with 1a/MAO catalyst in toluene proceed in living manner at low monomer concentration and sub-zero temperatures [3]. Our results tend to show that termination and transfer reactions are absent at 0 °C and even not significant at 20°C, at 0.8 M or at lower hex-1-ene concentrations when performing the polymerization in chlorobenzene. Surprisingly, even at higher monomer concentration, 1.8 M, poly(hex-1-ene)s exhibit narrow molar mass distribution at 0 °C, although  $M_w/M_n$  values regularly increase with hex-1-ene concentration indicating some contribution of side reactions (Table 1, entry 1 and 10-14). Another interesting result concerns 1b/MAO catalytic system that also produces poly(hex-1-ene) with narrow molar mass distribution which has not been observed previously. This behavior can be accounted to the

Table 2

Comparison of experimental and theoretical  $M_n$  values of poly(hex-1-ene) prepared by 1a/MAO initiator in chlorobenzene

| [HEX],<br>moll <sup>-1</sup> | <i>T</i> , °C | $M_n^{\exp}$ , kgmol <sup>-1</sup> | P.I. | $M_{\rm n}^{\rm theor},$<br>kgmol <sup>-1</sup> | $M_{\rm n}^{\rm exp}/M_{\rm n}^{\rm theor}$ |
|------------------------------|---------------|------------------------------------|------|---|---|
| 0.4                          | 0             | 95                                 | 1.10 | 42  | 2.3   |
| 0.8                          | 0             | 150                                | 1.15 | 86  | 1.7   |
| 1.8                          | 0             | 262                                | 1.16 | 145   | 1.8   |
| 0.8                          | 10            | 218                                | 1.14 | 134   | 1.6   |
| 0.8                          | 20            | 268                                | 1.18 | 157   | 1.7   |
| 0.8                          | 20            | 278                                | 1.15 | 159   | 1.7   |

 $M_n^{\text{theor}} = [\text{HEX}]/[I] * Y_w * M_0$ , where [I] is concentration of initiator,  $Y_w$  conversion,  $M_0$  molar mass of hex-1-en, P.I. polymolecularity index.



Fig. 3. Time dependence of monomer conversion and  $\ln([M]_0/[M])$  for hex-1-ene polymerization initiated by **1a**/MAO at 0°C in chlorobenzene, [Ni] = 1 mM, Al/Ni = 250.

positive effect of polar chlorobenzene in the stabilization of active sites  $^2$ .

In agreement with these observations polymerization kinetics performed by dilatometry (see Fig. 3 for example) show that monomer consumption follows an internal first order law. This is indicative of a system in which the formation of active species is rapid with respect to the propagation and with negligible termination reaction until relatively high conversions. Assuming this kinetic behavior as a general feature of these systems, we have plotted Fig. 4, the dependence of polymerization



Fig. 4. Dependence of activity (first hour reaction) on monomer concentration for hex-1-ene polymerization initiated by 1a/MAO at 0 °C in chlorobenzene, [Ni] = 200  $\mu$ M, Al/Ni = 250.

activity (first hour of reaction) on the initial concentration of hex-1-ene. Increase of initial monomer concentration results in a decrease of the activity indicating an apparent negative monomer order for the polymerization. A reduction of the polymerization activity caused by a decrease of solvent polarity at increasing monomer concentration can be ruled out since a same activity dependence was reported previously in toluene [11]. The monomer order determined to be -0.3 is in good agreement with the previously published value -0.2 [11].

The interpretation of this behavior, proposed by Peruch et al. [11], stands on the contribution of two different propagation active centers arising from the chain walking mechanism and exhibiting different reactivities. These two species were identified as β-substituted alkyl and the primary alkyl nickel complexes (noted  $C_1$  and  $C_6$  respectively in Scheme 2). The primary alkyl specie  $C_6$ , formed by chain walking, with a structure close to polyethylene propagating centers, was assumed as the more active. Since the overall reactivity increases when decreasing monomer concentration (negative monomer order), this would mean that the  $C_6$  propagating centers are present in higher proportion at low monomer concentration, in relation to higher contribution of the chain walking process. This will be further examined to the light of poly(hex-1-ene) microstructure.

A relatively similar behavior was also previously reported by Simon et al. [13] for ethylene polymerization: a negative monomer order was observed at high monomer concentration whereas a positive order was found in

<sup>&</sup>lt;sup>2</sup> The solvent effect on initiator stability is presently under investigation by means of UV–VIS spectroscopy which was previously shown to be an efficient tool for monitoring of active species formation and stability [11,12].



Scheme 2. Mechanism of  $\alpha$ -olefin polymerization catalyzed by nickel and palladium diimine complexes.

the low monomer concentration domain. However, ethylene polymerization mechanism is quite different. Insertion can occur into primary and secondary (formed by chain walking) metal–alkyl bonds, but both yield primary alkyl complexes as active species, contrarily to  $\alpha$ olefins. The presence of latent catalytic species formed by coordination of more than one monomer molecule to the metal center and which proportion increases at higher monomer concentration was proposed as an explanation in the case of ethylene polymerization.

Typical spectra of highly branched polyolefins obtained by palladium and nickel catalysts are presented



Fig. 5. Typical 300 MHz <sup>1</sup>H-NMR spectrum of poly(hex-1-ene) prepared by catalyst 1a/MAO; [HEX] = 0.8 M, 0 °C, chlorobenzene; CDCl<sub>3</sub>, 30 °C.

<sup>13</sup>C-NMR spectra of a branched polyethylene prepared with complex **2b** was used as reference to characterize the different poly(hex-1-ene) structures. In the polyethylene reference the characteristic signals for different alkyl branches are the following (see Fig. 6): methyl (1B1 at 20.07 ppm), ethyl (1B2 at 11.14 ppm), propyl (1B3 at 14.42 ppm), primary butyl (2B4 at 23.37 ppm), secondary butyl (A' and B' at 19.49 ppm and 11.65 ppm), amyl (3B5 at 32.67 ppm) and longer branches (3B6+ at 32.22 ppm). Analysis of poly(hex-1ene) prepared with initiator **1a**/MAO indicates the presence predominantly of methyl (1B1) and primary butyl branches (2B4). We can also conclude that ethyl, propyl, secondary butyl and longer branches are absent. The poly(hex-1-ene) structure can be explained in terms of regiospecificity of hex-1-ene insertion and chain-end isomerization. First, a significant proportion of normal 1,2-hex-1-ene insertion, characterized by primary butyl branches, directly followed by a new monomer insertion is taking place. However, 1,2-monomer insertion can be also accompanied by metal center migration leading to 2,6-hex-1-ene enchainment, as indicated by the formation of methyl branches. Besides, 2,1-monomer insertion is generally followed by chain-migration, prior a new monomer insertion, and results almost exclusively to 1,6-hex-1-ene enchainment. These results are in agreement with the reaction mechanism shown in Scheme 2.

Comparison of poly(hex-1-ene) spectra prepared by nickel **1a**/MAO system (Fig. 6, spectrum B) and palladium complex **2b** (Fig. 6, spectrum C) reveals an opposite ratio of methyl/but-1-yl branches which shows that in the case of 1,2-monomer insertions, contribution of chain walking is more important with the palladium catalyst. Poly(hex-1-ene) prepared by Ni initiator 1**a**/MAO

Fig. 6. 500 presup13C-NMR spectra of polyethylene prepared by catalyst **2b** (A) and poly(hex-1-ene) prepared by catalyst **1a**/MAO (B, entry 6) and **2b** (C, entry 4); CDCl<sub>3</sub>, 30 °C.





Scheme 3. Formation of long branches in hex-1-ene polymerization catalyzed by palladium diimine complex.

(spectra B) shows the same intensities of 2B4 and 1B4+ signals. Thus, we can conclude that 1B4+ peak is contributed almost exclusively by methyl from butyl branches and assign it like 1B4. In poly(hex-1-ene) prepared with Pd complex 2b (spectra C) we can further observe the presence of longer branches (4B6+ at 29.63 ppm, 3B6+ at 32.20 ppm, 2B5+ at 22.95 ppm). The intensity of 1B4+ peak is significantly higher than 2B4 indicating that 1B4+ peaks belongs not only to butyl branches but is also contributed by methyl from longer branches. Similar microstructures were observed in poly(octadec-1-ene) and block copolymer of octadec-1-ene and ethylene [5]. Nevertheless, in these cases, the discrimination between longer branches formed by chain walking and hexadecyl branches issued from 1,2monomer insertion could not be achieved by <sup>13</sup>C-NMR analysis. The presence of longer branches in poly(hex-1-ene) prepared with palladium derivative compared to nickel catalyst could be explained by much faster and farther migration of Pd center along the polymer chain. Due to the fact that the monomer cannot insert into secondary alkyl bonds, the metal center must walk to the branch ends forming primary alkyl species capable of further propagation: thus, no ethyl and propyl branches are formed. Further insertion at these "end of branches" growing centers followed by chain migration can lead to formation of short methyl and butyl branches or longer branches after 1,2- or 2,1-insertion, respectively, as shown in Scheme 3.

This tendency of palladium to promote higher migration is also confirmed by the lower number of total branches as measured by <sup>1</sup>H-NMR analysis (Table 1).

A strong influence of the diimine ligand structure on the isomerization process is also noticed (Table 1, entries 1 and 2). Increase of the reaction temperature (complex **1a**, Table 1, entries 1, 5–7) yields an increase of the chain-end isomerization, as already reported [7,14]. This result is in agreement with an apparent higher activation energy for the chain walking process than for the monomer insertion.

The variation of poly(hex-1-ene) branching with decreasing hex-1-ene concentration is shown in Fig. 7. As could be seen, there is a dependence of the number of poly(hex-1-ene) branches on monomer concentration. The total number of poly(hex-1-ene) branches decreases with the monomer concentration decrease, in line with a higher contribution of the chain walking mechanism and an increase of the proportion of 1,6-monomer insertion leading to formation of polyethylene sequences. This is in agreement with a higher proportion and contribution of  $C_6$  centers to the polymerization at low monomer concentration, as proposed by Peruch et al. [11].

The influence of the poly(hex-1-ene) branching degree on its thermal properties was also examined by



Fig. 7. Dependence of branching on initial monomer concentration in hex-1-ene polymerization initiated by 1a/MAO at 0°C in chlorobenzene, [Ni] =  $200 \mu M$ , Al/Ni = 250.


Fig. 8. DSC traces of poly(hex-1-ene)s obtained at  $0^{\circ}$ C with 1a/MAO with initial monomer concentration 5.8 M (entry 14), 0.8 M (entry 1) and 0.2 M (entry 10).

DSC analysis on selected samples. DSC records are shown in Fig. 8. As expected, the less branched products, obtained at higher monomer concentration, show lower glass-transition temperature.

#### 4. Conclusion

The polymerization of hex-1-ene catalyzed by diimine palladium and nickel based catalyst has been investigated. The influence of the structure of catalyst and polymerization conditions on initial polymerization rate (activity for the first hour) and structural polymer characteristics were analyzed and correlated. The results are in line with the hex-1-ene polymerization data published earlier. The polymerization initiated by 1a/MAO exhibits living characteristics such as linear increase of molar mass with the initial ratio monomer/Ni and narrow molar mass distribution even at high hex-1-ene concentrations. Living-like behavior was observed also for Ni initiator 1b/MAO. This can be accounted to a stabilizing effect of chlorobenzene on active species. Molar masses of poly(hex-1-ene)s are, however, higher than predicted, indicating a low initiator efficiency due to incomplete activation of the nickel derivative. The negative order with respect to hex-1-ene concentration, reported for several nickel based systems, was confirmed for hex-1ene polymerization initiated by 1a/MAO. This unusual behavior can be correlated to the modification of the nature and proportion of propagating species with the monomer concentration in relation with the change in the poly(hex-1-ene) microstructure. Further work is in progress to evaluate the influence of the olefin structure on this very peculiar kinetic behavior.

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**P2** 

## Effect of Ligand Backbone Substituents of Nickel α-diimine Complexes on Livingness/controllability of Olefin Polymerization: Competition between Monomer Isomerization and Propagation

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**ABSTRACT:** Four  $\alpha$ -diimine nickel complexes ((Ar-N=C(R)-C(R)=N-Ar)NiBr<sub>2</sub>; R=H, CH<sub>3</sub>, cyclohexane-1,2diyl, naphthalene-1,8-diyl, Ar = 2,6-*i*-Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-) were investigated in propene and hex-1-ene polymerization in order to identify the limits of backbone substituent R size needed to provide living/controlled  $\alpha$ -olefins polymerization by the sufficient suppression of  $\beta$ -H elimination transfer. Propagation kinetics measurements, molar mass on monomer conversion dependencies and reinitiation tests were used to evaluate the livingness of hex-1-ene polymerization. Interestingly, living/controlled hex-1-ene polymerization was observed in the case of all diimine derivatives including the one bearing only hydrogen atom in backbone positions. Unexpectedly, in the case of catalysts bearing H and CH<sub>3</sub> backbone substituents, we observed the unusual isomerization of hex-1-ene into internal hexenes in parallel with its polymerization. Nevertheless, by subtracting the amount of monomer consumed in isomerization side reaction, polymerization still keeps the features of living/controlled process.

**KEYWORDS:** living/controlled polymerization, isomerization, olefin, nickel, kinetics

## INTRODUCTION

 $\alpha$ -diimine nickel and palladium complexes are attractive catalysts that are able to produce polyolefins with a different microstructure than classical Ziegler-Natta or metallocene catalysts.<sup>1</sup> The reason for this lies in a specific mechanism of these catalysts in which insertion reaction is accompanied by so-called chain-walking. The consequence of chain-walking is a possibility to prepare branched polymer by ethylene homopolymerization only. On the contrary,  $\alpha$ olefins polymerization leads to less branched polymer that would be expected from regular 1,2-enchainment of a monomer.<sup>2</sup> The extent of chain-walking can be tuned by reaction temperature, monomer concentration and catalyst structure. Moreover, both  $\alpha$ -diimine nickel palladium and complexes can initiate living/controlled olefin polymerization.<sup>3,4</sup> Therefore, these complexes enable the preparation of precise polyolefins with (i) narrow molar mass distribution (ii) predetermined molar mass and (iii) controlled short chain branching. Such polyolefins are valuable model materials for investigating of solution or melt behavior of macromolecules with different branching.<sup>5,6</sup> This knowledge helps to provide structure-property relationship of commercial grade polyolefins such as linear low



density polyethylene or ethylene-propylene copolymer.

While the modification of aniline moieties of  $\alpha$ diimine ligands has received considerable attention,<sup>2,7-20</sup> much less works have dealt with the effect of the backbone substituents on polymerization behavior of corresponding Ni  $\alpha$ diimine complexes.<sup>17,21-25</sup> In the field of living/controlled olefin polymerization nickel complexes with acenaphthenequinone based diimine ligand backbone were used at most.<sup>3,12,13</sup> Indeed, these catalysts were found to be highly active, provided good control over molar mass and enabled the synthesis of block copolymers.

In our previous paper, we have shown that for livingness/controllability of the polymerizations the bulkiness of diimine ligand ortho aryl substituent is not as crucial as proposed in early studies<sup>3</sup> and that even ligands with methyl initiate well controlled groups can polymerization of hex-1-ene.<sup>7</sup> However, no detail research on the backbone substitution effect on livingness/controllability has been reported. Our previous study suggested that even diimine ligand with methyl backbone groups (Figure 1, complex 2) could lead to controlled polymerization system.<sup>26</sup> Recently, a synthesis of thermoplastic elastomers based on block copolymers of dodecen-1-ene with ethylene was described using 2/Et<sub>2</sub>AICI showing the possibility to copolymerize even ethylene in controlled way by nickel diimine complexes.<sup>27</sup>

Here, we continue with a systematic structureactivity relationship study of nickel diimine complexes in order to identify the limits of ligand structure design within which it is possible to achieve living/controlled olefin polymerization. Four nickel complexes **1-4** with different backbone substituent size were synthesized for this purpose (Figure 1) and investigated in propene and hex-1-ene polymerization. Unexpected monomer isomerization competing with controlled propagation is described in the case of less bulky backbone groups.



FIGURE 1 Ni  $\alpha$ -diimine complexes used in this work

## EXPERIMENTAL

## Materials

All manipulations with air-sensitive compounds were done using standard Schlenk techniques. Nitrogen (SIAD, 99.999%) was purified by passing through a column packed with Cu-catalyst and molecular sieves to remove traces of oxygen and water. Chlorobenzene (p.a., Penta) was refluxed over CaH<sub>2</sub> and distilled under nitrogen. Hex-1-(99%, Aldrich) was dried ene over sodium/potassium alloy and distilled under nitrogen. Trans-hex-2-ene was dried over CaH<sub>2</sub> and vacuum transferred prior to polymerization. Methylaluminoxane (MAO) (10 wt% solution in toluene, Aldrich) was used as received. Nickel complexes were synthesized according to reported procedures.<sup>1,17</sup> Catalysts were dosed as a solid directly to the polymerization vessel or in the form of chlorobenzene solutions that were stored at 5 °C.

## **Hexenes polymerization**

Polymerizations were carried out under dry nitrogen in magnetically stirred 15mL glass ampoules. The ampoules with chlorobenzene, hex-1-ene (or hex-2-ene), and catalyst were placed in a bath kept at a desired temperature and tempered for 15 min. The polymerization was initiated by the addition of MAO solution. After the desired reaction time the polymerization was terminated by pouring the reaction mixture to 250 mL of ethanol with 10% HCl, washed by ethanol and dried 24 h at 50 °C under vacuum.

Reinitiation tests were carried out by addition of second portion of monomer after the consumption of initial monomer feed.

## GC method for hex-1-ene polymerization kinetics investigation

Method described in literature<sup>28</sup> was used using cyclohexane in the feed as an internal standard. Polymerization was prepared in the same way as described above with exception of addition of 1 ml of cyclohexane after monomer addition. 1-2 ml samples were withdrawn from the reaction mixture in course of the polymerization, quenched by pouring into 10 mL ethanol, and decanted or centrifuged in order to isolate a precipitated polymer. Liquid phases were transferred to 2 ml vials equipped with septum and measured by gas chromatography immediately. GC analysis was performed on Varian CP 3800 chromatograph using capillary column HP Ultra 1 (PDMS, 50 m length, inner diameter 0.32 mm, film thickness 0.52 µm) at 60 °C and 3 ml.min<sup>-1</sup> nitrogen flow.

## **Propene polymerization**

Polymerizations of propene were carried out in chlorobenzene in a magnetically stirred jacketed 100 mL glass reactor under 110 kPa dynamic pressure. The solvent and the catalyst solution were injected against propene flux and the reactor was cooled to a desired temperature. The polymerization was initiated by the addition of MAO solution. After 90 min the polymerization was guenched by the addition of 1 mL of 10% HCl in methanol, and the polymer was precipitated in 300 mL of methanol. The polymer was separated and dried 24 h at 50 °C under vacuum.

## **Polymer characterization**

The microstructure of polyhexenes and polypropylenes was determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies. NMR spectra of polymers were measured on 500 MHz Bruker Avance DRX 500 spectrometer in CDCl<sub>3</sub> solution (15–20% w/v) at 30 °C. <sup>13</sup>C NMR INVGATE spectra of polyhexenes were collected typically 15–20 h (5000–7000 scans) using 90° pulse and

relaxation delay of 10 s to allow the quantification of methyl carbon signals. Chemical shifts were referenced internally to the major backbone methylene carbon resonance, which was taken at 30.00 ppm from TMS. Interpretation of <sup>13</sup>C NMR spectra was based on previously published assignments.<sup>29,30</sup>

The total number of branches per 1000 carbon atoms (N) was determined by integrating methyl proton signals with respect to signals of all protons in <sup>1</sup>H NMR spectrum and calculated using the formula:

$$N = \frac{2(I_{\rm CH_3})}{3(I_{\rm CH+CH_2+CH_3})} \times 1000$$

The precision of N determination by  $^1\text{H}$  NMR is 2-3%.

Molar masses were determined using Waters Breeze chromatographic system equipped with RI detector operating at 880 nm and multi-angle laser light scattering (MALLS) miniDawn TREOS from Wyatt operating at 658 nm. Separations were performed with two columns (Polymer Laboratories Mixed C) at 35 °C in THF at an elution rate of 1 mL min<sup>-1</sup>. The dn/dc value  $0.078 \pm 0.002$  mL g<sup>-1</sup> in THF at 35 °C was used for both poly(hex-1-ene)s and polypropylenes.<sup>7</sup>

## **RESULTS AND DISCUSSION**

## Hex-1-ene polymerization

Four nickel  $\alpha$ -diimine complexes **1-4** (Figure 1) with different backbone substituents were prepared and tested in the polymerization of hex-1-ene after activation with 200 eq. of MAO (Table 1). This ratio was chosen based on previous experiments which showed that for similar nickel diimine complexes activated by MAO a plateau of activity appears at MAO/Ni higher than 50.<sup>31,32</sup> Ortho-aryl substituents of all studied complexes were fixed to be isopropyl groups as in a benchmark complex **3**, which is one of the first and the most common nickel



| Run | Cat. | T<br>(°C) | Time<br>(h) | Y <sub>p,grav</sub> <sup>a</sup><br>(%) | Y <sub>p,GC</sub> <sup>b</sup><br>(%) | M <sub>n,exp</sub> <sup>c</sup><br>(kg mol <sup>-1</sup> ) | Ð °  | Mn <sup>th d</sup><br>(kg mol⁻¹) | N <sup>e</sup> |
|-----|------|-----------|-------------|---|---------------------------------------|--|------|----------------------------------|----------------|
| 1   | 1    | -10       | 22          | 87                                      | 91                                    | 132  | 1.08 | 121                              | 165            |
| 2   | 1    | 25        | 1           | 64                                      | 65                                    | 85   | 1.36 | 90                               | 117            |
| 3   | 2    | -10       | 22          | 92                                      | 95                                    | 155  | 1.01 | 125                              | 113            |
| 4   | 2    | 25        | 1           | 45                                      | 49                                    | 88   | 1.01 | 65                               | 102            |
| 5   | 2    | 25        | 22          | 61                                      | 66                                    | 149  | 1.02 | 82                               | 109            |
| 6   | 3    | -10       | 22          | 90                                      | 98                                    | 386  | 1.21 | 147                              | 136            |
| 7   | 4    | -10       | 22          | 5                                       | <1                                    | 35   | 1.05 | 7                                | 146            |

TABLE 1 Hex-1-ene polymerization initiated by 1-4/MAO in chlorobenzene

hex-1-ene/Ni = 1600–1800, [Ni] = 0.8 mM, Al/Ni = 200, total volume 15 ml. <sup>*a*</sup> Gravimetric conversion of monomer to polymer. <sup>*b*</sup> GC conversion of monomer to polymer. <sup>*c*</sup> Molar mass and dispersity determined by SEC-MALLS. <sup>*d*</sup> Theoretical molar mass  $M_n^{th}$  = polymer mass/mol<sub>N</sub>. <sup>*e*</sup> Number of branches per 1000 C atoms obtained from <sup>1</sup>H NMR.

α-diimine complex used for living/controlled olefin polymerization<sup>3</sup> and which also showed high degree of control in our previous works.<sup>7,26,32</sup> The solubility of complexes in chlorobenzene, used as a polymerization media, decreases in the order 3 > 4 ~ 2 > 1. Complex 1 had very low solubility in both chlorobenzene and dichloromethane and therefore was dosed as a solid directly to the polymerization ampoule. The suspension of 1 in monomer and solvent turned to completely homogeneous solution upon addition of MAO, thus ensuring all complex 1 being engaged in the polymerization.

Complexes 1-3 afforded poly(hex-1-ene) in high yield after 22 h at -10 °C. However, complex 4 with mid-sized cyclohexanediyl backbone substituent surprisingly yielded only very low amount of polymer. This might be due to a nonplanar conformation of cyclohexanediyl backbone in 4 compared to complexes 1 and 3 and more bulky structure of 4 compared to 2. Poly(hex-1-ene) prepared by all complexes showed very narrow molar mass distribution suggesting controlled polymerization. а Comparison of poly(hexe-1-ene)s experimental and theoretical molar masses showed a good agreement in case of complexes 1 and 2. For complex 3 molar mass is substantially higher than the expected one showing low MAO activation efficiency for **3** at given experimental conditions. Incomplete activation of naphthalenedivl substituted complex 3 was already observed in previous works<sup>7,28,31</sup>. For complex 4  $M_{n,exp}/M_{n,th}$  is equal to 5 suggesting that only 20% of the nickel precursor might be activated. Whereas the increase of reaction temperature from -10 to 25°C leads to broadening of poly(hex-1-ene) molar mass in the case of the least bulky 1 (Table 1, run 1 vs. run 2), complex 2 with methyl backbone groups affords a polymer with very narrow molar mass even at 25 °C (Table 1, run 3 vs. runs 4, 5). As expected, increased polymerization temperature led to increase in reaction rate and moderate monomer conversion were achieved already after 1 h (Table 1, runs 2 and 4).

## Kinetics of hex-1-ene polymerization

In order to study the reactivity of complexes **1-4** more into detail, we performed a kinetic study of hex-1-ene polymerization using gaschromatography to monitor the monomer consumption. Polymerizations were carried out at -10 °C to suppress transfer and termination reactions to minimum. The order of the polymerization rates does not correspond with ligand backbone substituent bulkiness, **1**/MAO being the fastest, followed by **3**/MAO and **2**/MAO (Figure 2). Similar indirect relationship between ligand bulkiness and polymerization rate was observed previously<sup>7,13,17</sup> and explained by two opposite effects: (i) decrease of rate by restricted monomer access to metal center in the case of more bulky ligands and (ii) increase of rate by decrease of insertion barrier caused by destabilization of ground state of monomer insertion by more bulky ligands. In the case **4**/MAO surprisingly all hex-1-ene monomer was consumed within first hour of polymerization.



**FIGURE 2** GC conversion-time dependence of hex-1-ene conversion to poly(hex-1-ene) (full symbols) and to internal hexenes (empty symbols) during hex-1-ene polymerization initiated by 1/MAO (diamonds, run 1), 2/MAO (circles, run 3), 3/MAO (triangles, run 6) and 4/MAO (squares, run 7) at -10 °C. Al/Ni = 200, T = -10 °C, hex-1-ene/Ni= 1600–1800, [Ni] = 0.8 mM.

Owing to use GC to follow kinetics of monomer consumption we were able to identify a surprising side reaction – the isomerization of hex-1-ene to internal hexenes (Figure 2, empty symbols). According to GC-MS *cis/trans*-hex-2ene and *cis/trans*-hex-3-ene were formed. To our best knowledge, such a behavior has not yet been observed for any nickel diimine catalyst. Hex-1-ene isomerization was previously

described by analogous Pd diimine complex with methyl backbone substituents leading to 40% of internal hexenes in 2 h at room temperature.<sup>4</sup> The formation of isomers is clearly connected with ligand backbone substituent size in the series of complexes 1, 2 and 3. Whereas in the case of naphthalenediyl substituted complex 3 no isomer formation was observed, complex 2 slowly generated internal hexenes during 20 h polymerization run and in the case of 1 significant isomerization took place in first hour of the experiment leading to formation internal hexenes in around 20% yield at -10 °C (Figure 2). The behavior of complex 4 is again specific as a very fast isomerization occurs converting more than 95% of hex-1-ene into internal isomers in one hour. Fast isomerization is therefore a true reason for very low poly(hex-1-ene) yield in case of complex 4 as hex-1-ene is accessible for the polymerization only at the very beginning of the reaction.

Interestingly, the concentration of internal hexenes decreased during the hex-1-ene polymerization by **1** at -10 °C (Figure 2) showing the possibility of **1**/MAO to slowly polymerize even internal hexenes or isomerize them back to hex-1-ene. Slow polymerization of internal hexenes was proved with Pd diimine complex<sup>4</sup> and Ni diimine complexes were shown to polymerize *trans*-2-butene.<sup>33</sup> Relatively low extent of isomerization in the case of complexes **1-3** at -10 °C is reflected in good correlation between monomer conversion values obtained gravimetrically and from GC measurements (Table 1).

To see the effect of temperature on the extent of isomerization reactions, hex-1-ene was polymerized by **1** and **2** at 25 °C (Figure 3). Due to the increase of propagation rate and rate of isomerization the time of experiment was 1 hour. Formation of internal hexenes reached almost 40% for **1** and their slow insertion to the polymer chain can be seen. While the isomers formation was almost not detectable in the case of complex **2** at -10 °C after 1 h, at room temperature **2** formed around 5% of isomers.





**FIGURE 3** GC conversion-time dependence of hex-1-ene conversion to poly(hex-1-ene) (full symbols) and to internal hexenes (empty symbols) during hex-1-ene reaction with 1/MAO (diamonds) and 2/MAO (triangles) at 25 °C in chlorobenzene. Al/Ni = 200, [hex-1-ene] = 1.1 M, [Ni] = 0.8 mM

MAO cocatalyst is well known for its instability and change of activation efficiency in time. Therefore, we intended to study the effect of MAO aging on catalyst 1/MAO polymerization behavior with focus on potential effect of MAO quality on the extent of monomer isomerization. For this purpose compared we the polymerization carried out at -10 °C with 200 eq. of fresh MAO (Table 1, run 1) with the one in which we used MAO solution stored in fridge for more than two years (Figure 4, diamonds vs. triangles). Indeed 5-10% shift of curve of conversion to polymer to lower conversion values was observed when using aged MAO. Simultaneously, higher amounts of internal hexenes were formed in this experiment (Figure 4, empty symbols). As the older MAO solution contains lower amount of MAO molecules able of activation process we decided to model this situation by using of fresh MAO at Al/Ni = 20 ratio (Figure 4, circles). In the initial phase of the polymerization more than 50% of hex-1-ene was turned into internal hex-1-enes exceeding even isomerization extent observed at room temperature (Figure 3). This shows an important effect of MAO quality on the sensitivity of 1/MAO to catalyze hex-1-ene isomerization at the expense of its conversion to poly(hex-1-ene).



**FIGURE 4** GC conversion-time dependence of hex-1-ene conversion to poly(hex-1-ene) (full symbols) and to internal hexenes (empty symbols) during hex-1-ene polymerization at -10°C initiated by **1** activated by fresh MAO (diamonds Al/Ni = 200; circles Al/Ni = 20) and aged MAO (triangles, Al/Ni = 200). Hex-1-ene/Ni = 1600-1800, [Ni] = 0.8 mM, chlorobenzene.

In order to assess the reaction order to monomer and controllability of the reaction we constructed first-order plots for hex-1-ene polymerization catalyzed by 1-3/MAO at -10°C (Figure 5). At this conditions hex-1-ene isomerization is almost negligible in case of complexes 2 and 3. However, a significant proportion of isomerization is observed for complex 1. Therefore, the instantaneous hex-1ene concentration [M] was calculated by subtracting the amount of hex-1-ene converted to both polymer and isomers from initial hex-1ene concentration [M]<sub>0</sub> to eliminate the overlapping effect of isomerization and propagation kinetics:

$$[M] = [M]_0 \times (1 - Y_{isomer} - Y_{polymer})$$

where  $Y_{isomer}$  and  $Y_{polymer}$  is conversion of hex-1ene into internal isomers and polymer, respectively.

Linear dependencies of  $ln([M_0]/[M])$  on time (Figure 5) shows that the propagation reaction is first order with respect to monomer concentration in the case of all catalyst **1-3**/MAO suggesting the controlled character of polymerizations.



**FIGURE 5** Semi-logarithmic dependence of  $ln([M_0]/[M])$  on time in hex-1-ene polymerization initiated by **1-3**/MAO at -10 °C in chlorobenzene. Hex-1-ene/Ni= 1600-1800, [Ni] = 0.8 mM, Al/Ni = 200

## Livingness of hex-1-ene polymerization

Narrow molar mass distributions and kinetics measurements suggested living/controlled character hex-1-enes polymerizations of initiated by 1-3/MAO. To further check the livingness of polymerization in the case of complexes 1 and 2 we performed a monomer resumption test. As checked by the absence of hex-1-ene in mixture by GC, an initial feed of hex-1-ene was completely consumed by both polymerization and isomerization in 22 h at -10°C for both 1/MAO and 2/MAO. Conversion

to polymer was 86% and 83% for 1/MAO and 2/MAO, respectively. After this period a sample of polymer was taken for SEC analysis and the same amount (~400 eq. of monomer to Ni) was added to the reaction mixture. After additional 22 h the conversion of second monomer feed to polymer was 76% for both catalysts. SEC analysis of polymers showed increase of molar mass well corresponding to monomer/initiator ratio and conversion to polymer (Figure 6). Poly(hexe-1ene)s dispersity values remained very narrow after consumption of second monomer feed showing a good stability of growing centers in case of both 1/MAO and 2/MAO. Higher molar mass shoulder in SEC chromatogram of polymer obtained by 2/MAO corresponds to doubled molar mass fraction and is probably caused by partial coupling of polymer chains during the termination as it is observed for methanol terminated polymerization catalyzed by analogous Pd complexes.<sup>34</sup>



FIGURE 6 SEC chromatograms of poly(hex-1ene)s obtained by 1/MAO (upper chart) and



**2**/MAO (lower chart) after 22 h of polymerization (right peaks) and after reinitiation by addition of a second portion of monomer after additional 22 h of polymerization (left peaks). T = -10 °C, [Ni] = 1.0 mM, Al/Ni = 200, hex-1-ene/Ni = 400+400.

To further prove a living/controlled character of hex-1-ene polymerizations initiated by **1-3/**MAO molar masses and dispersity values were plotted over conversion to polymer (Figure 7). For all three systems **1-3/**MAO these dependencies are highly linear (Figure 7, charts A-C), which,

together with dispersity values remaining well below 1.10 during the whole period of polymerization, documents the living/controlled character of these polymerizations. In the case of **2**/MAO we evaluated hex-1-ene polymerization also at 25 °C. Even in this case, the polymerization is highly controlled (Figure 7, chart D). Experimental molar masses in the case of **1**/MAO are close to theoretical ones showing a quantitative activation of **1** by MAO. Activation of complexes **2** and **3** by MAO was incomplete (50–80%) as earlier observed for **3**.<sup>7,28,31</sup>



**FIGURE 7** Dependence of number average molar mass (diamonds) and dispersity (circles) on monomer conversion to polymer in hex-1-ene polymerization initiated by **1-3**/MAO at -10 °C (chart A-C) and by **2**/MAO at 25 °C (chart D) in chlorobenzene. [C6] = 1.1-1.2 M, [Ni] = 0.7-0.8 mM, [AI]/[Ni] = 200

To conclude, narrow molar mass distribution of prepared polymers, linear first-order plots, monomer resumption test and linear molar mass vs. conversion plot shows that when subtracting the amount of hex-1-ene consumed by isomerization, the remaining hex-1-ene undergoes well controlled living polymerization even in the case of complexes **1** and **2** bearing small backbone substituents.

## Poly(hex-1-ene) microstructure

Branching of poly(hex-1-ene)s is influenced by the ligand backbone structure (Table 1). Lowest degree of chain walking is expected in the case of sterically least hindered complexes due to easier monomer coordination to metal center which blocks the vacant position needed for the formation of  $\beta$ -agostic alkyl-nickel species, the intermediates in chain walking mechanism.<sup>2</sup> At -10 °C catalyst 1/MAO affords poly(hex-1-ene) with 165 branches per 1000 C atoms, the value one could expect from regular 1,2-insertions (167 br./1000 C) suggesting the suppressing effect of low ligand size and also the influence of low reaction temperature, both being the factors decreasing the extent of chain walking. The same catalyst undergo more chain walking at 25°C when poly(hex-1-ene) with 117 br./1000 C is formed. However, a detailed branching analysis by quantitative <sup>13</sup>C NMR spectroscopy (Figure 8, Table 2) shows that even the polymer prepared at -10 °C by 1 is not regular poly(hex-1-ene), bearing only butyl branches, but contains also all other types of short branches. This reflects a significant extent of chain walking during the polymerization. The presence of high amount of methyl branches witnesses a significant proportion of 1,2-insertion followed by chain walking resulting in 2,6-enchainment of hex-1ene (Scheme 1, route B). Poly(hex-1-enes) prepared by complexes 2, 3 and 4 resulted in more rearranged polymer structure (Table 1, run. 3, 6, 7), however, no clear correlation between the ligand size and branching degree can be drawn. Complex 2 resulted in the most rearranged (~30% of 1,6 enchainment) poly(hex-1-ene) with 113 br./1000 C at -10 °C.

Interestingly the temperature dependence of chain walking for **2** is much less pronounced compared to **1** as an increase of temperature from -10 to 25 °C resulted only in a minor decrease of branching from 113 to 102–109 br./1000 C, (Table 1, run 3 vs. run 4 and 5).



**FIGURE 8** <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) spectra of poly(hex-1-ene)s prepared by complexes 1 (upper, run 1), 2 (middle, run 3) and 3 (lower, run 6) activated by MAO at -10 °C

**TABLE 2** Branching distribution in poly(hex-1ene)s prepared by complexes **1**/MAO (Table 1, run 1), **2**/MAO (run 3) and **3**/MAO (run 6) at -10 °C determined by <sup>13</sup>C NMR.

| Bronch type                   | Number of branches per 1000 C atoms |       |       |  |  |  |
|-------------------------------|-------------------------------------|-------|-------|--|--|--|
| ы апонттуре                   | run 1                               | run 2 | run 3 |  |  |  |
| Methyl                        | 31                                  | 14    | 21    |  |  |  |
| Ethyl                         | 9                                   | 0     | 0     |  |  |  |
| Propyl                        | 10                                  | 1     | 1     |  |  |  |
| Butyl                         | 93                                  | 77    | 95    |  |  |  |
| Hexyl and longer              | 7                                   | 4     | 9     |  |  |  |
| Total br./1000 C <sup>a</sup> | 162                                 | 104   | 138   |  |  |  |

<sup>a</sup> Obtained from integration of all methyl signals regarding to signal intensity of the whole <sup>13</sup>C NMR spectra



<sup>13</sup>C NMR spectroscopy confirms the highest degree of poly(hex-1-ene) microstructure rearrangement in the case of complex 2 as reflected in the lowest amount of butyl branches (Table 2, run 3). It is worthy to mention that the poly(hex-1-ene)s prepared by 2 and 3 do not contain almost any ethyl or propyl branches referring to either regular 1,2-insertion (forming butyl branch, Scheme 1, route A), 1,2-insertion followed by chain walking (forming methyl branch, route B) or 2,1-insertion followed by chain walking (no branch is formed, route C). Chain walking thus usually leads to the migration of metal to the end of branch or chain end to form a primary alkyl-nickel bond which undergo next monomer insertion. On the contrary, poly(hex-1-ene) prepared by 1 contains a significant amount of ethyl (11.10 ppm) and propyl (14.80 ppm) branches which could be

caused by chain walking and monomer insertion to secondary alkyl-nickel bonds (Scheme 1, routes D and E). Such insertions are known to be highly disfavored despite a small proportion of  $\alpha$ olefin insertion into secondary alkyl-nickel bonds was observed in previous works using 3/MAO.<sup>30,35</sup> Therefore, more plausible explanation for the presence of ethyl and propyl branches in poly(hex-1-ene) prepared by 1 can be connected again with an important extent of hex-1-ene isomerization to internal hexenes which could provide these branches. For all catalysts **1-3**/MAO the formation of hexyl or longer branches in poly(hex-1-ene) is further observed which can be explained by 2,1insertion followed by chain-walking leading to 1,6-enchainment and another 2,1-insertion followed by chain walking back to polymer chain (Scheme 1, route F).



SCHEME 1 Mechanism of branch formation in hex-1-ene polymerization initiated by 1-3/MAO

To verify the hypothesis that ethyl and propyl branches in poly(hex-1-ene) prepared by **1** could be formed by insertion of internal hexenes we performed a model polymerization of *trans*-hex-2-ene. Hex-2-ene polymerization initiated by complexes **1**, **2** and **3** was investigated at monomer/Ni = 1000 and -10 °C and monitored by GC (Table 3). No hex-1-ene was detected in

the reaction mixture suggesting it was not formed by isomerization of hex-2-ene (in accordance with lower thermodynamic stability of terminal olefin) or it was immediately polymerized. The rate of hex-2-ene polymerization was much slower than in the case of hex-1-ene polymerization, therefore the polymerization time was prolonged to 44 h.



Poly(hex-2-ene) obtained by 1 was obtained in 65% yield. The other two complexes resulted in much lower yield (7% for 2 and 20% for 3). Interestingly polymers obtained by complexes 2 and **3** have very narrow molar mass distribution suggesting the controlled character of polymerization even in the case of hex-2-ene. However, molar masses are much higher than expected ones, showing a low catalyst efficiency. Regular 2,3- or 3,2-insertion of hex-2-ene leads to a secondary alkyl-nickel bond which has a very low probability of another insertion of internal olefin due to steric reasons. The need of a rearrangement of the last monomer unit prior to next insertion is reflected also in overall branching degree which is of about 50% of values corresponding to the direct hex-2-ene insertions.

<sup>13</sup>C NMR analysis of poly(hex-2-ene) obtained by **1** (and also by **3**) clearly shown the presence of large amount of propyl and ethyl branches (Figure 9). The formation of propyl and ethyl branches results from 2,3-insertion followed by chain walking of nickel center to the end of branches forming primary alkyl-Ni bond capable of further monomer insertion (Scheme 3, routes G and H). Relatively high amount of methyl branches is formed by 3,2-insertion of hex-2-ene followed by chain walking leading finally to 2,6insertion (route I). Butyl branches were detected only in a small amount confirming negligible **TABLE 3** Hex-2-ene polymerization initiated by **1-3**/MAO

isomerization of hex-2-ene to hex-1-ene. They can be also formed by 1,2-insertion of hex-2-ene resulting from 3,2-insertion followed by chain walking (route J). Thus, the presence of ethyl and propyl branches in poly(hex-1-ene) prepared by 1 can be explained by the incorporation of internal hexenes formed by hex-1-ene isomerization during its simultaneous polymerization.

Ethyl and propyl branches in poly(hex-1-ene) structure were observed previously also in the N,N'-bis(2,6-dimethylphenyl)-2,3case (naphthalene-1,8-diyl)-1,4-diazabuta-1,3-diene) nickel dibromide (5) activated by MAO and tentatively explained by hex-1-ene insertion into secondary alkyl-Ni bonds.<sup>7</sup> Therefore, we revisited this catalytic system and monitored the hex-1-ene polymerization by GC which proved again the formation of internal hexenes. Hex-2ene polymerization by 5/MAO confirmed the presence of ethyl and propyl branches in the obtained polymer which can be explained in the same way as for complex 1 (Scheme 2, Figure 9). The sterical effect of diimine ligand substituents is therefore not only important to suppress chain transfer reactions during olefin polymerization but also protects the olefin from its isomerization, another important side reaction.

| Run | Cat  | Y <sub>p,grav</sub> <sup>a</sup><br>(%) | M <sub>n,exp</sub> <sup>b</sup><br>(kg mol <sup>-1</sup> ) | Ð    | Mn <sup>th d</sup><br>(kg mol⁻¹) | N <sup>e</sup> | Branching distribution <sup>e</sup> |    |    |    |
|-----|------|---|--|------|----------------------------------|----------------|-------------------------------------|----|----|----|
|     | Cal. |   |  |      |                                  |                | Ме                                  | Et | Pr | Bu |
| 8   | 1    | 65                                      | 26   | 1.74 | 37                               | 159            | 66                                  | 33 | 41 | 5  |
| 9   | 2    | 3                                       | 14   | 1.15 | 2                                | -              | -                                   | -  | -  | -  |
| 10  | 3    | 20                                      | 89   | 1.19 | 13                               | 166            | 71                                  | 34 | 36 | 5  |

*trans*-hex-2-ene/Ni = 1000, [Ni]= 0.2 mM, Al/Ni = 200, T = -10 °C,  $t_p$  = 44 h, chlorobenzene, total volume 15 ml. <sup>*a*</sup> Gravimetric conversion of monomer to polymer. <sup>*b*</sup> Molar mass and dispersity determined by SEC-MALLS. <sup>*c*</sup> Theoretical molar mass  $M_n^{th}$  = polymer mass/mol<sub>Ni</sub>. <sup>*d*</sup> Number of branches per 1000 C atoms obtained from <sup>1</sup>H NMR. <sup>*e*</sup> Number of branches per 1000 C atoms obtained from <sup>13</sup>C NMR



**SCHEME 2** Mechanism of branch formation in hex-2-ene polymerization initiated by **1**/MAO and **3**/MAO



**FIGURE 9** <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) spectra of poly(hex-1-ene)s prepared by complexes **1** (upper, run 8), **3** (middle, run 10) and **5** (lower) activated by MAO at -10 °C

## **Propene polymerization**

Complexes **1-4** activated with 200 eq. of MAO were also used in atmospheric pressure propene polymerization at -10 °C in chlorobenzene (Table

4). In the case of propene polymerization, isomerization does not change the monomer structure and therefore cannot play such an important role as in the case of hex-1-ene polymerization. The order of complexes activity 3 > 2 > 4 > 1 determined from polymer yield after 90 min is different than in the case of hex-1-ene polymerization. This again shows the complex relationship between the ligand bulkiness and complex activity which is influenced by steric restriction of ligand for monomer coordination and by changes of propene insertion barrier. Much higher polymerization activity of **3**/MAO can also be ascribed to more electronwithdrawing effect of naphthalenediyl substituent which increases electrophilicity of nickel center and favors the coordination of propene to it. Polypropylenes obtained by all investigated catalysts have higher molar mass than the expected one showing on incomplete activation of nickel precursors by MAO.

**TABLE 4** Propylene polymerization initiated by **1**-**4**/MAO in chlorobenzene

| Run | Cat. | TOF<br><sup>a</sup><br>(h⁻¹) | M <sub>n,exp</sub> <sup>b</sup><br>(kg mol⁻<br>¹) | Đ <sup>b</sup> | Mn <sup>th c</sup><br>(kg mol⁻<br>¹) | N <sup>d</sup> |
|-----|------|------------------------------|---|----------------|--------------------------------------|----------------|
| 11  | 1    | 175                          | 24  | 2.53           | 11                                   | 291            |
| 12  | 2    | 820                          | 68  | 1.08           | 56                                   | 253            |
| 13  | 3    | 2160                         | 197   | 1.09           | 137                                  | 265            |
| 14  | 4    | 294                          | 84  | 1.03           | 19                                   | 215            |

T = -10 °C, p(propene) = 110 kPa, 90 min, [Ni] = 0.5 mM, Al/Ni = 200, total volume 30 ml. <sup>a</sup> Turnover frequency as calculated from the mass of polymer obtained. <sup>b</sup> Molar mass and dispersity determined by SEC-MALLS. <sup>c</sup> Theoretical molar mass  $M_n^{th}$  = polymer mass/mol<sub>Ni</sub>. <sup>d</sup> Number of branches per 1000 C atoms obtained from <sup>1</sup>H NMR

Polypropylene prepared by 1/MAO has very broad molar mass distribution which shows a significant influence of side reactions. This is probably caused by more planar geometry of active species formed from the complex 1, in which small hydrogen backbone atoms do not sterically interact with isopropyl groups on aryl rings and do not force the aryl rings to turn to almost perpendicular orientation to the diimine ligand plane as it is in the case of more bulky



backbone substituents.<sup>36</sup> Thus, insufficient hindering of nickel axial positions cannot effectively prevent the formation of bis-olefin hydrido nickel species, which is considered as transfer-reaction transition state, and consequently leads to high extent of transfer reactions.<sup>2</sup> Complexes 2-4 with more bulky backbone substituents form polypropylene with very narrow molar mass distribution showing almost complete suppression of transfer reactions and controlled character of the polymerization. The extent of chain walking is also influenced by catalyst structure. Based on <sup>1</sup>H NMR data the lowest rearrangement is observed for the complex 1 with the lowest ligand bulkiness. This is in agreement with expectations as relatively more accessible nickel center can easily coordinate propene molecule and interrupt the chain walking process which can proceed only on β-agostic alkyl-nickel species.<sup>2</sup> No clear relationship between the ligand bulkiness and chain walking can be found for the other complexes displaying 25-35% rearrangement of the polymer chains caused by 1,3-insertion of propene.

## CONCLUSIONS

Nickel diimine complexes 1-4 activated by MAO afforded poly(hex-1-ene)s and poly(propylene)s with narrow molar mass distribution. The size of diimine backbone substituents is crucial for occurrence of hex-1-ene isomerization to internal hexenes, the reaction which competes with hex-1-ene propagation. Isomerization is very intensive in hex-1-ene polymerization catalyzed by 4/MAO preventing the formation of poly(hex-1-ene) in high yield. For complexes 1 and 2 isomerization is highly temperature dependent, much more pronounced at room temperature. MAO quality or Al/Ni ratio are shown to be another parameter significantly influencing the extent of isomerization reaction. Complex 3 does not produce any detectable amount of isomers at any tested conditions. When assuming only the monomer accessible to polymerization (not consumed the by isomerization) the hex-1-ene polymerization by **1** and **2** is well controlled and living as documented by linear first-order plots, possibility to reinitiate the polymer growth by addition of fresh monomer and linear molar mass vs. conversion dependence. Together with the possibility to influence polymer branching by ligand structure these catalysts allow the preparation of poly(hex-1-ene) with controlled molar mass, narrow molar mass distribution and controlled amount of branches. Propene polymerization by 1 at -10 °C leads to polymer with broad molar mass distribution showing a higher importance of ligand backbone bulkiness in the case of the smaller monomer molecule, more active in transfer reactions. The microstructure of polymers was investigated by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and mechanistic model explaining the formation of observed branching was proposed. Unusual presence of ethyl and propyl branches observed in poly(hex-1-ene) prepared by complex **1** is caused by the incorporation of internal hexenes into the polymer.

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# Living/controlled olefin polymerization initiated by nickel diimine complexes: The effect of ligand *ortho* substituent bulkiness

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#### ABSTRACT

Polymerization of hex-1-ene and propene initiated by several methylalumoxane-activated diimine complexes was critically investigated. Effect of bulkiness of *ortho* aryl diimine substituents on extent of transfer reactions was examined. All of the complexes allowed us to prepare poly(hex-1-ene) with a very narrow molar mass distribution, molar mass being controlled by stoichiometry in a broad range of reaction conditions. Poly(hex-1-ene)s with molar mass between 15 and 220 kg mol<sup>-1</sup> and dispersity ( $M_w/M_n$ ) between 1.01 and 1.20 were prepared by varying the catalyst, temperature and monomer concentration. Livingness of hex-1-ene polymerization was demonstrated for the first time for nickel complex bearing ethyl *ortho* aryl substituents by reinitiation of chain growth upon addition of a new portion of monomer. Complexes with *ortho* methyl substituents did not allow complete reinitiation of chain growth and despite its good control over molar mass cannot be classified as a living polymerization. Polypenpylene with narrow molar mass distribution could not be prepared using complexes with methyl substituents.

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#### 1. Introduction

Presently, polyolefins represent the largest group of commodity polymers. Considerable attention (both academic and industrial) is therefore focused on the development of new catalytic systems and polymerization processes [1]. To improve material properties of polyolefins, it is highly desirable to develop methods allowing one to control polymer chain parameters, such as molar mass and its distribution, stereoregularity or degree of branching. One of the most powerful methods to control polymer architecture [2] is living/controlled olefin polymerization [3]. Significant number of catalytic systems based on both early and late transition metal complexes was used for living/controlled olefin polymerization in last two decades [4]. Nickel diimine complexes represent an attractive group of such catalysts due to their high polymerization activity, lower oxophility, easy synthesis and the fact that they do not need high Al/metal ratios for catalyst activation [5].

Original Brookhart's publication claims a living character of alk-1-ene polymerization for methylalumoxane (MAO) and modified methylalumoxane activated acenaphthenchinone derived nickel complexes bearing bulky isopropyl and *tert*-butyl substituents in *ortho* aryl positions of ligand (Fig. 1, **1** and **2**) [6].

Living/controlled polymerization behavior was described for low polymerization temperatures and low monomer concentrations only, which limits the practical use of these complexes.

Marked suppression of transfer reactions by increased bulkiness of ligand *ortho* substituents was explained by hindering of axial positions of diimine complexes that prevents formation of the



Fig. 1. Structure of nickel diimine complexes applied.

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transfer-reaction transition state represented by pentacoordinated *bis*-olefin hybrid species (Fig. 2) [5].

Living polymerization of hexe-1-ene initiated by the 2/MAO system was examined more in detail by Peruch [7]. Formation of poly(hex-1-ene) with narrow molar mass distribution was observed for the monomer/initiator ratio (M/I) up to 1500 at -10 °C; within this limit, a reinitiation of polymerization was achieved. Later, we observed living/controlled hex-1-ene polymerization behavior using 1/MAO system in chlorobenzene in much broader range of reaction temperatures and monomer concentrations, affording poly(hex-1ene)s with narrow molar mass distribution [8]. Recently investigated hex-1-ene and dec-1-ene polymerizations catalyzed by MAO activated complex 1 and its analogue with -NCS leaving groups instead of Br anions gave polyolefins with narrow molar mass distribution at 0-30 °C [9]. Effect of pressure on hex-1-ene polymerization catalyzed by the bulky complex **1** and its analogue with butandione backbone was investigated by Suzuki et al. Poly(hex-1-ene)s with narrow molar mass distribution were prepared at room temperature only at ambient pressure. However, polymer yields were not quantitative and molar masses were significantly higher than those expected from the given *M*/*I* ratio [10]. Other more sophisticated catalytic systems bearing bulky diimine substituents were reported to show the living polymerization behavior [11,12]. High temperature stability of catalyst and good control over molar mass and dispersity was achieved by Guan using cyclophane diimine Ni complex for α-olefin polymerization [11]. In addition to the control over polymer molar mass and its distribution, chiral nickel diimine complexes reported by Coates allow one to control the regioselectivity at low temperatures [12]. However, a better chain growth and microstructure control of these systems are paid by more complicated diimine ligand synthesis and often much lower catalyst activity.

Poly(hex-1-ene) with low dispersity was also prepared with the 3/MAO system having methyl diimine substituents in ortho and para positions at  $-11 \,^{\circ}C$  [13]. An analogous nickel complex, namely {bis[N,N'-(4-tert-butyl-diphenylsiloxy-2,6-dimethylphenyl)imino]acenaphthene} dibromonickel (6), bearing methyl groups in ortho positions and bulky tert-butyldiphenylsiloxyl group in para position yielded polypropylene and poly(hex-1-ene) with narrow molar mass distribution at -11 °C and even at 16 °C [14]. Di- and triblock copolymers of hex-1-ene and propene were prepared by the complex **6** at -15 °C. In case of both complexes **3** and **6**, however, the polymerization was not carried out to complete monomer conversion to prove unambiguously the living character of polymerization. Further, hex-1-ene homopolymerizations initiated by 3 and 6 displayed the linear increase of molar mass with time. This would rather suggest a deviation from the living/ controlled polymerization behavior which is usually demonstrated



Fig. 2. Structure of the transfer reaction transition state.

by the linear dependence of molar mass on the monomer conversion in closed systems, assuming first order kinetics with respect to the monomer concentration. Similarly, Sivaram recently questioned the existence of the true living polymerization behavior of the 1/MAO system in hex-1-ene polymerization by kinetic observations [15]. Noticeable chain transfer reactions were observed for M/l above 1500 and temperatures above 20 °C.

In this paper, we report on a critical comparative study of living/ controlled olefin polymerization behavior of five basic nickel diimine complexes (Fig. 1, **1–5**) in a broad range of reaction conditions with focus on the effect of *ortho* aryl substituents bulkiness on the extent of transfer reactions. Several criteria defining living/controlled polymerization behavior are examined to show the level of polymerization controllability and classify the catalysts either as "living" or only "controlled" according to IUPAC and ACS recommendations [3]. Possibilities to tune also polymer microstructure by catalyst choice are outlined.

#### 2. Experimental section

#### 2.1. Materials

All manipulations with air-sensitive compounds were done using standard Schlenk techniques. Nitrogen (SIAD, 99.999%) was purified by passing through a column packed with Cu-catalyst and molecular sieves to remove traces of oxygen and water. Chlorobenzene (p.a., Penta) was refluxed over CaH<sub>2</sub> and distilled under nitrogen. Hex-1-ene (99%, Aldrich) was dried over sodium/ potassium alloy and distilled under nitrogen. MAO (10 wt% solution in toluene, Aldrich) was used as received. Nickel complexes were synthesized and purified according to reported procedures [6]. Purity of diimine ligands was proved by <sup>1</sup>H NMR and catalyst purity was checked by elemental analysis. Solutions of catalysts in chlorobenzene were stored at 5 °C.

#### 2.2. Polymerization procedures

#### 2.2.1. Hex-1-ene polymerization

Polymerizations were carried out under dry nitrogen in magnetically stirred 15 mL glass ampoules. Ampoules with chlorobenzene, hex-1-ene and initiator were placed in a bath kept at a desired temperature and tempered for 15 min. Polymerization was initiated by addition of MAO solution. After desired reaction time the polymerization was quenched by 1 mL of 10% HCl in MeOH, polymer was precipitated in 200 mL of MeOH and shortly dried at 50 °C under vacuum. The polymer product was dissolved in toluene, the solution centrifuged and polymer in the supernatant was reprecipitated in a large excess of MeOH in order to remove the insoluble rest of catalytic system. Polymer was separated and dried at 50 °C under vacuum until constant weight. To get the dependence of molar mass on the degree of monomer conversion, samples (3–4 mL each) were taken from the polymerization mixture (total volume 30 mL), quenched by pouring into acidified EtOH, separated and dried under vacuum. Kinetics of hex-1-ene polymerization was followed in 10 mL dilatometer equipped with a PTFE valve.

#### 2.2.2. Propene polymerization

Polymerizations of propene were carried out in chlorobenzene in a magnetically stirred jacketed 100 mL glass reactor under 110 kPa dynamic pressure. The solvent and the catalyst solution were injected against propene flux and reactor was cooled to -10 °C. Polymerization was initiated by addition of the MAO solution. After 90 min the polymerization was quenched by addition of 1 mL of 10% HCl in MeOH, and polymer was precipitated in 300 mL of MeOH. After short drying, polymer was dissolved in toluene, centrifuged and polymer in the supernatant was reprecipitated in a large excess of MeOH to remove the insoluble rests of catalytic system. Polymer was separated and dried at 50 °C under vacuum until constant weight was achieved.

#### 2.3. Polymer characterization

The microstructure of poly(hex-1-ene)s and polypropylenes was determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies. NMR spectra of polymers were measured on 500 MHz Bruker Avance DRX 500 spectrometer in CDCl<sub>3</sub> solution (15–20% w/v) at 30 °C.

<sup>13</sup>C NMR INVGATE spectra of poly(hex-1-ene)s were collected typically 15–20 h (5000–7000 scans) using 90° pulse and relaxation delay of 10 s to allow the quantification of methyl carbon signals. Chemical shifts were referenced internally to the major backbone methylene carbon resonance, which was taken at 30.00 ppm from TMS. Interpretation of <sup>13</sup>C NMR spectra was based on APT and previously published assignments [16–18]. The nomenclature used is that of Usami [16] and Galland [18]. On labels *xBy*, By is a branch of length *y* carbons, *x* is the carbon being discussed, and the methyl at the end of the branch is numbered 1. Thus, the second carbon from the end of a butyl branch is 2B4. *xBy*+ refers to the branches of length *y* and longer.

The total number of branches per 1000 carbon atoms (N) was determined by integrating methyl proton signals with respect to signals of all protons in <sup>1</sup>H NMR spectrum and calculated using the formula:

$$N = \frac{2(I_{\rm CH_3})}{3(I_{\rm CH+CH_2+CH_3})} \times 1000$$

Molar masses were determined using Waters Breeze chromatographic system equipped with RI detector operating at 880 nm and multi-angle laser light scattering (MALLS) miniDawn TREOS from Wyatt operating at 658 nm. Separations were performed with two columns (Polymer Laboratories Mixed C) at 35 °C in THF at an elution rate of 1 mL min<sup>-1</sup>. The values of dn/dc of polyolefins in THF at 35 °C were obtained by two methods:

- (1) Off-line determination for 5 selected poly(hex-1-ene) samples with low and high degree of branching using Wyatt Optilab REX detector at 658 nm by measuring polymer solutions in THF at 4 concentration levels  $(dn/dc = 0.078 \pm 0.002 \text{ mL g}^{-1})$ .
- (2) On-line measurements [19] using Waters 2414 refractometer at 880 nm giving  $dn/dc = 0.077 \pm 0.001$  mL g<sup>-1</sup> for large series of poly(hex-1-ene)s and  $dn/dc = 0.079 \pm 0.001$  mL g<sup>-1</sup> for 6 polypropylene samples.

Average dn/dc value  $0.078 \pm 0.002 \text{ mL g}^{-1}$  in THF at 35 °C was found to be independent of the degree of polymer branching and used for SEC-MALLS evaluation of both poly(hex-1-ene)s and polypropylenes. Dn/dc value determined by us is consistent with previously reported  $dn/dc = 0.078 \pm 0.003 \text{ mL g}^{-1}$  obtained for THF solutions of highly branched polyethylenes prepared by Pd diimine catalyst at 932 nm [20]. Another dn/dc value for poly(hex-1-ene) prepared by **2**/MAO was reported to be 0.068 mL g<sup>-1</sup> in THF at 633 nm [7].

#### 3. Results and discussion

#### 3.1. Polymerization of hex-1-ene

Polymerization of hex-1-ene was investigated using nickel diimine complexes differing in their substituents in *ortho* aryl positions (Fig. 1, 1–5). In addition to bulky isopropyl and *tert*-butyl

substituents (Fig. 1, 1,2) described in original Brookhart's paper [6], complexes with smaller (methyl and ethyl) *ortho* aryl substituents were also employed (Fig. 1, 3–5). Chlorobenzene was chosen as a solvent for the reaction due to a better solubility of nickel complexes as compared to toluene. Further, good solubility of high molar mass poly(hex-1-ene)s in chlorobenzene prevents the separation of polymer-containing less polar phase from relatively more polar catalyst phase at low polymerization temperatures, as was observed using dichloromethane and cyclohexane.

To assess the living character/controllability of polymerization, the values of the number of polymer molecules produced per one catalyst molecule, NPM/N(Ni), were calculated. To achieve correct values of this parameter, an exact value of polymer molar mass must be known, for which we used the SEC-MALLS method. We have observed in many experiments that rubbery poly(hex-1-ene)s, separated by standard precipitation of polymerization mixture to acidified methanol, encapsulated significant amounts (up to 20 wt.%) of MAO decomposition products. This would bring an error not only into monomer conversion values calculated from the weight of polymer but also into values of specific refractive index increment (dn/dc) used for the molar mass determination. Consequently, the values of NPM/N(Ni) derived from monomer conversion and molar mass would be erroneous. For that reason, polymers were purified by centrifugation as described in Experimental section. The NPM/N(Ni) values can finally be influenced by inactive impurities in the catalyst precursor which is difficult to characterize properly by, e.g., NMR spectroscopy due to its paramagnetic character. Purity of the nickel complexes was satisfactory, as found by elemental analysis; despite a relatively low sensitivity of the method we have estimated the maximum error of the NPM/ N(Ni) determination to be smaller than 10%.

#### 3.1.1. Control of molar mass

Our previous observations [8], namely that the hex-1-ene polymerization with complex **1** activated by MAO has a living/ controlled character even at higher temperatures and higher monomer concentrations than initially claimed by Brookhart, led us to investigate the polymerization in detail in a broad range of reaction conditions. Thus, polymerizations were carried out between -10 °C and 25 °C in a wide *M/I* ratio range (200–3200) to explore reaction conditions under which living/controlled polymerization can be achieved (Table 1).

Results of the hex-1-ene polymerization with complexes 1 and 2 activated by MAO are in agreement with Brookhart's observations that nickel catalysts with bulky ortho aryl substituents of diimine ligand are capable to initiate the living/controlled polymerization of  $\alpha$ -olefins [6]. Polymerizations reach almost complete monomer conversion after several hours and polymers prepared show a very narrow molar mass distribution within the whole temperature and M/I ratio range explored. Increase of dispersity is observed only in experiments with the highest M/I ratio (3200) suggesting an important role of the transfer reactions to monomer (Table 1, run 3 and 8). The NPM/N(Ni) values for both catalytic systems are lower than one, suggesting incomplete activation of complexes 1 and 2 by MAO, as reported in literature [7,8,15]. However, for complex 1 only a small part (<10%) of catalyst species is inactive and molar masses are in good agreement with the predicted values. In the case of complex 2, catalyst efficiency is more decreased and approximately 20% of Ni complex remains untransformed to growing centers. An increased importance of the transfer reactions at high M/I ratio is reflected, beside in higher dispersity values, also in an increase of NPM/N(Ni) values above one (run 3 and 8). The effect of temperature on the increase of the transfer reaction extent is not detectable and the NPM/N(Ni) values remain almost constant between -10 °C and 25 °C.

 Table 1

 Polymerization of hex-1-ene initiated by 1–5/MAO in chlorobenzene.

| Run | Catalyst | M/I  | Tp   | $Y_w^a$         | $M_n^{b}$       | $M_{\rm w}/$ | NPM/               | N <sup>d</sup> |
|-----|----------|------|------|-----------------|-----------------|--------------|--------------------|----------------|
|     | -        |      | [°C] | [%]             | $[kg mol^{-1}]$ | $M_n^{b}$    | N(Ni) <sup>c</sup> |                |
| 1   | 1        | 200  | -10  | 93              | 16.5            | 1.05         | 0.94               |                |
| 2   |          | 800  | -10  | 92              | 67.0            | 1.01         | 0.92               | 127            |
| 3   |          | 3200 | -10  | 73 <sup>e</sup> | 149.3           | 1.36         | 1.31               | 140            |
| 4   |          | 800  | 0    | 93 <sup>e</sup> | 70.8            | 1.01         | 0.88               |                |
| 5   |          | 800  | 25   | 95 <sup>e</sup> | 73.1            | 1.01         | 0.87               |                |
| 6   | 2        | 200  | -10  | 80              | 17.3            | 1.01         | 0.77               |                |
| 7   |          | 800  | -10  | 93              | 71.6            | 1.05         | 0.87               | 109            |
| 8   |          | 3200 | -10  | 85              | 205.5           | 1.26         | 1.11               | 138            |
| 9   |          | 800  | 25   | 95              | 79.8            | 1.06         | 0.80               | 98             |
| 10  | 3        | 200  | -10  | 94              | 19.3            | 1.04         | 0.82               |                |
| 11  |          | 800  | -10  | 96              | 61.4            | 1.11         | 1.05               | 148            |
| 12  |          | 3200 | -10  | 94              | 116.7           | 1.57         | 2.16               | 161            |
| 13  |          | 800  | 0    | 97              | 56.3            | 1.18         | 1.15               |                |
| 14  |          | 800  | 25   | 96              | 49.7            | 1.32         | 1.29               | 113            |
| 15  | 4        | 200  | -10  | 58              | 15.7            | 1.14         | 0.65               |                |
| 16  |          | 800  | -10  | 75              | 60.1            | 1.13         | 0.85               | 146            |
| 17  |          | 3200 | -10  | 97              | 144.5           | 1.50         | 1.86               |                |
| 18  |          | 800  | 0    | 82              | 55.6            | 1.20         | 0.99               |                |
| 19  |          | 800  | 25   | 84              | 45.9            | 1.50         | 1.26               |                |
| 20  | 5        | 200  | -10  | 87              | 18.7            | 1.08         | 0.87               | 108            |
| 21  |          | 800  | -10  | 90              | 66.0            | 1.08         | 1.09               | 131            |
| 22  |          | 3200 | -10  | 84              | 219.7           | 1.12         | 1.05               | 148            |
| 23  |          | 800  | 0    | 95              | 68.2            | 1.04         | 0.99               | 120            |
| 24  |          | 200  | 25   | 98              | 21.6            | 1.09         | 0.76               | 84             |
| 25  |          | 800  | 25   | 92              | 62.7            | 1.13         | 1.01               | 100            |

 $[\mathrm{Ni}]$  = 1.0 mM, Al/Ni = 200, polymerization time 5 h, total volume 10 mL  $^a$  Monomer conversion.

 $^{\rm b}$  Number average molar mass  $(M_{\rm n})$  and dispersity  $(M_{\rm w}/M_{\rm n})$  determined by SEC-MALLS.

<sup>c</sup> NPM/N(Ni) = polymer mass/(mol<sub>Ni</sub>· $M_n$ ).

<sup>d</sup> Number of branches per 1000 C atoms determined by <sup>1</sup>H NMR spectroscopy.

<sup>e</sup> Polymerization time 1 h.

Recently, living/controlled behavior was reported for the hex-1ene polymerization initiated by MAO-activated complexes 3 and 6 bearing only small methyl substituents in ortho aryl positions [13,14]. We have therefore decided to investigate polymerizations of hex-1ene with complex 3 in more detail in the next step. In addition to that, other two complexes **4** and **5** bearing methyl and ethyl groups (Fig. 1) have been prepared to prove the potential of diimine complexes with small aryl substituents to catalyze the polymerization in living/controlled manner. Both 4 and 5 were substituted in ortho aryl positions that probably represent the crucial substitution pattern for protecting growing centers against transfer reactions. Results of the hex-1-ene polymerization initiated by 3-5/MAO in a wide range of reaction temperatures and monomer concentrations are collected in Table 1. Polymers with narrow dispersity were obtained below 0 °C and below 800 for all the three complexes 3-5 activated by MAO indicating controlled polymerization. In case of complexes 3 and 4 with methyl substituents, considerable extent of side reactions, i.e. loss of control, could be observed at high *M*/*I* and at room temperature, as indicated by the increase of dispersity and NPM/N(Ni) values (Table 1, run 12, 14, 17, 19). Further, complex 4 showed lower monomer conversions, suggesting the increased contribution of termination reactions. Similarly as for 1 and 2, complexes 3 and 4 often feature incomplete activation by MAO and, despite their increased sensibility to transfer reactions, yield fewer polymer chains than could be expected from the amount of catalyst molecules present (Table 1, runs 10, 15, 16).

Interestingly, complex **5** bearing relatively small ethyl substituents has been proved to perfectly control the polymerization even at a very high M/I ratio (3200) as well as at room temperature (Table 1, runs 20–25). Moreover, catalyst efficiency of the **5**/MAO

system, expressed by NPM/N(Ni), is the best of all the catalysts under study. Within the limits of experimental error, the number of polymer molecules is in agreement with the number of catalyst molecules and does not change in a broad range of experimental conditions. This makes **5**/MAO a very suitable system for the preparation of uniform polyolefins with tailored molar mass in the range of  $10^3$  to  $10^5$  g mol<sup>-1</sup>, as controlled by the pre-set *M/I* ratio in the feed. The negligible extent of transfer reactions indicates that the bulkiness of ethyl groups is sufficient to suppress the transfer-reaction transition state formation (Fig. 2).

#### 3.1.2. Livingness of polymerization

The possibility to prepare low dispersity polymers is only one of living/controlled polymerizations attributes and reflects high initiation rate as compared to propagation, as well as only insignificant amount of irreversible transfer and termination reactions [3]. To investigate more properly the livingness/controllability of olefin polymerization initiated by complexes with sterically less demanding ligands, we followed the dependence of molar mass on monomer conversion in hex-1-ene polymerization initiated by **4**/MAO and **5**/MAO at -10 °C and at M/I = 800 (Fig. 3). In both cases,



**Fig. 3.** Dependence of number average molar mass and dispersity  $(M_w/M_n)$  on monomer conversion in hex-1-ene polymerization initiated by **4**/MAO (upper chart) and by **5**/MAO (lower chart). T = -10 °C, [hex-1-ene] = 0.8 M, [Ni] = 1 mM, Al/ Ni = 200, Total volume 30 mL,  $M_n$ (theoretical) = conversion \*m(hex-1-ene)/mol<sub>Ni</sub>.

the controllability of polymerization is confirmed by the fact that the plot of molar mass vs. hex-1-ene conversion is linear and molar mass distribution does not broaden in course of polymerization. The complex **4** yields poly(hex-1-ene) with higher dispersity values as compared to 5. For the complex 4, the experimentally determined molar masses are higher than those calculated from the M/I ratio. The average efficiency of **4** is 0.82 implying incomplete activation by MAO. In case of complex 5, experimental molar masses are in good agreement with those predicted. A higher deviation of molar masses from the theoretical values is observed at lower conversions for both complexes. This could be caused by a higher experimental error of determination of polymer yield from relatively small samples at lower monomer conversions, or, alternatively, by a slower initiation, as observed previously by Sivaram for complex **1** [15]. However, dispersity values of poly(hex-1-ene)s prepared by any of the two initiation systems remain low and do not evolute in course of the whole experiment which indicates a fast initiation and a negligible extent of the transfer reactions at given conditions.

5020

To examine the polymerization livingness/controllability [15] and to compare polymerization activities of all complexes, we performed kinetic investigation by means of dilatometry (Fig. 4). At -10 °C all complexes showed first order kinetics with respect to monomer concentration at least up to 50% monomer conversion as proved by the linearity of the plot of  $\ln[M_0]/[M_t]$  vs. polymerization time; this indicates that propagation is accompanied by only negligible transfer and termination reactions. At higher conversions, however, complex 4 has shown substantional deviation from the linearity, suggesting the presence of termination reactions. Propagation rates of complexes 1-5 are not directly proportional to the bulkiness of their ligands. Two opposing effects can be responsible for this behavior. On the one hand, a higher steric demand restrains the access of the monomer to the growing center, decreasing thus the polymerization rate. On the other hand, a bulky ligand lowers the insertion barrier by destabilizing the ground state of monomer insertion relative to transition state which results in an increase of the propagation rate. A similar behavior was previously observed for ethylene and propylene polymerizations catalyzed by nickel diimine complexes [20,12b]. The complex 2 derived from monosubstituted bulky 2-tert-butylaniline displayed a significantly



**Fig. 4.** Semilogarithmic dependence of  $ln[M_0]/[M_t]$  on time in hex-1-ene polymerization initiated by **1–5**/MAO at -10 °C in chlorobenzene. [hex-1-ene] = 0.8 M, [Ni] = 1 mM, Al/Ni = 200.

lower polymerization rate than the complexes derived from disubstituted anilines with substituent size varying from small methyl to large isopropyl groups.

Finally, to show the possibilities to control olefin polymerization initiated by diimine complexes **4** and **5**, we tried to reinitiate the growth of the chain by adding a second portion of monomer, after all monomer in the original feed had been consumed (Figs. 5 and 6). As is known, the nickel diimine catalysts are instable and decompose fast in absence of the monomer [7]. Thus, to protect most of growing centers, it is important to add the second portion of monomer shortly after the initial monomer feed is converted to polymer. This time period was estimated on the basis of dilatometry results. For the complex 4 (Fig. 5), molar mass is almost doubled after reinitiation but dispersity is increased and higher molar mass peak shows a tail of lower molar mass fraction indicating a certain extent of transfer and termination reactions. Therefore, the polymerization of hex-1-ene catalyzed by 4/MAO cannot be considered as the living one but as the controlled polymerization at the most. In the reinitiation experiment with complex 5 (Fig. 6), polymer molar mass was doubled almost exactly and dispersity remained very low as a consequence of a negligible extent of transfer reactions. Hex-1-ene polymerization catalyzed by 5/MAO can therefore be assigned as an exceptionally good example of living coordination polymerization at the current state of the knowledge in the field.

#### 3.2. Polymerization of propene

Polymerization of propene was investigated at ambient pressure using complexes **1–5** activated by 200 equiv. MAO in chlorobenzene at -10 °C (Table 2). The order of the propene polymerization activity for all of the complexes **1–5** is similar to that of propagation rates observed in the case of hex-1-ene (Fig. 4). The complexes **1** and **4** differing essentially in ligand bulkiness were found to have highest activities, confirming thus complexity of the reaction mechanism. The lowest activity was consistently observed for the complex **2** with monosubstituted diimine ligand. Compared to the hex-1-ene polymerization, propene polymerization is, in most cases, accompanied by a larger extent of transfer reactions, as indicated by higher dispersity values of polypropylenes prepared. This could be explained by a higher propensity of diimine



**Fig. 5.** SEC chromatograms of poly(hex-1-ene)s initiated by **4**/MAO and reinitiated by addition of a second portion of monomer after 5 h. T = -10 °C, [hex-1-ene] = 0.4 + 0.4 M, [Ni] = 1 mM, Al/Ni = 200.



**Fig. 6.** SEC chromatograms of poly(hex-1-ene)s initiated by **5**/MAO and reinitiated by addition of a second portion of monomer after 5 h. T = -10 °C, [hex-1-ene] = 0.4 + 0.4 M, [Ni] = 1 mM, Al/Ni = 200.

complexes to transfer to monomer as a consequence of an easier access of smaller propene molecule to growing center and subsequently higher probability to form transfer-reaction transition state (Fig. 2). Reasonably narrow molar mass distribution was observed for polypropylenes obtained by the bulky complexes 1 and 2, as reported previously by Brookhart [6]. The complexes 3 and 4 with small methyl substituents display substantially increased dispersity values. Extraordinary good suppression of the transfer was surprisingly observed in case of the catalyst 5 which yielded polypropylene with dispersity as low as 1.08. Comparison of NPM/ N(Ni) values for the complexes 1, 2, 3 and 5 revealed that the extent of transfer reactions is quite limited in spite of molar mass distribution broadening. However, NPM/N(Ni) values can be influenced by an incomplete activation of the catalysts by MAO. Hence, the only reliable indication of living/controlled behavior could be assigned to the complex 5, where a good correlation between the number of produced polymer chains and that of initiator molecules is accompanied by low dispersity values. In case of the complex 4, the NPM/N(Ni) value (1.80) indicates an important role of the transfer reactions.

#### 3.3. Control of microstructure

In addition to the control over polymer molar mass, simultaneous control of polymer microstructure represents another important challenge. A very good control over stereoselectivity by changing the reaction temperature in propylene polymerization

Table 2Polymerization of propene initiated by 1–5/MAO in chlorobenzene.

| Run | Catalyst | $A^{a}$        | $M_n^b$    | $M_{\rm w}/M_{\rm n}{}^{\rm b}$ | NPM/N(Ni) <sup>c</sup> | N <sup>d</sup> |
|-----|----------|----------------|------------|---------------------------------|------------------------|----------------|
|     |          | [kg mol · h ·] | [kg mol ·] |                                 |                        |                |
| 26  | 1        | 63.6           | 101.5      | 1.27                            | 0.94                   | 292            |
| 27  | 2        | 25.9           | 32.1       | 1.29                            | 1.21                   | 241            |
| 28  | 3        | 39.2           | 66.0       | 1.42                            | 0.89                   | 299            |
| 29  | 4        | 65.6           | 54.7       | 1.43                            | 1.80                   | 292            |
| 30  | 5        | 38.8           | 61.2       | 1.08                            | 0.95                   | 262            |

 $[\rm Ni]$  = 0.5 mM, Al/Ni = 200, T = -10 °C, p(propene) = 110 kPa, polymerization time 1.5 h, total volume 30 mL.

<sup>a</sup> Polymerization activity.

<sup>b</sup> Molar mass and dispersity  $(M_w/M_n)$  determined by SEC-MALLS.

<sup>c</sup> NPM/N(Ni) = polymer mass/(mol<sub>Ni</sub>· $M_n$ ).

<sup>d</sup> Number of branches per 1000 C atoms determined by <sup>1</sup>H NMR spectroscopy.

using chiral nickel diimine complexes was recently reported by Coates [12]. However, crystalline isotactic polypropylene is formed only at very low reaction temperatures which leads to relatively low polymerization activity and low molar mass of resulting polymers. Another strategy to control polymer microstructure could be used in the case of diimine catalysts, based on their natural sensitivity to undergo  $\beta$ -H elimination followed by a subsequent olefin reinsertion, so called chain-walking mechanism allowing the growing center to migrate along the polymer chain [5,21]. The extent of chain-walking can be influenced by reaction temperature, monomer concentration and catalyst structure. In case of longer  $\alpha$ -olefins, chain-walking leads to 1, $\omega$ - or 2, $\omega$ - monomer insertions. 1,  $\omega$ -insertions lead to straightening of chain and formation of linear "polyethylene-like" domains that are capable of crystallization [7,9]. The possibility to control polyolefin molar mass using several complexes differing significantly in the bulkiness of their ligands, as in the case of the complexes 1–5, gives us a new simple tool for synthesizing polymers controlled both in molar mass and microstructure. All poly(hex-1-ene)s and polypropylenes prepared by complexes 1-5 (Tables 1 and 2) are, as a consequence of chainwalking, less branched than would correspond to regular 1,2-monomer insertion, i.e. 167 branches/1000 C atoms for poly(hex-1-ene) and 333 branches/1000 C atoms for polypropylene. As seen from Table 1, the choice of the catalyst can significantly influence branching of the poly(hex-1-ene) chain under given reaction conditions (e.g. Table 1, run 7, 35% rearrangement vs. runs 11 and 16, 11% rearrangement). Moreover, due to a broad range of reaction temperatures and M/I ratios under which most of nickel complexes allow one to prepare polyolefins with controlled molar mass and low dispersity, it is possible to prepare poly(hex-1-ene) with even larger degree of rearrangement (run 24, 68% rearrangement). Similarly to poly(hex-1-ene)s, the degree of polypropylene rearrangement is affected by the bulkiness of diimine ligand (e.g. Table 2, run 27, 28% rearrangement vs. run 28, 10% rearrangement).

In the case of selected poly(hex-1-ene)s, more detailed structural analysis was performed by means of <sup>13</sup>C NMR spectroscopy (Fig. 7). Intensities of methyl signals, relaxed quantitatively under employed measurement conditions, are collected in Table 3 along with <sup>1</sup>H NMR data. The most abundant are butyl (e.g. 1B4+ at 14.39 ppm, 2B4 at 23.48 ppm) and methyl (1B1, 19.98 ppm) branches for all four poly(hex-1-ene)s samples. Poly(hex-1-ene) prepared by catalyst **4** (Table 3, run 16) surprisingly showed also the presence of ethyl (1B2, 11.12 ppm) and propyl (1B3, 14.83 ppm) branches despite the fact that this polymer shows, according to <sup>1</sup>H



**Fig. 7.** <sup>13</sup>C NMR spectra of poly(hex-1-ene)s prepared by MAO activated catalysts **1** (Table 1, run 2), **2** (run 7), **4** (run 16), **5** (run 21) at -10 °C. [hex-1-ene] = 0.8 M, [Ni] = 1 mM, Al/Ni = 200.

#### Table 3

| microstructure of poly(new r che/s prepared by 1,2,1,0/microstructure) |
|--|
|--|

| Catalyst | Run | N <sup>a</sup> | %1,2-ins. <sup>b</sup> | 1B1 <sup>c</sup> | 1B4 <sup>c</sup> | 1B1/1B4 |
|----------|-----|----------------|------------------------|------------------|------------------|---------|
| 1        | 2   | 127            | 76                     | 17               | 82               | 0.21    |
| 2        | 7   | 109            | 65                     | 56               | 33               | 1.70    |
| 4        | 16  | 140            | 84                     | 63               | 51               | 1.24    |
| 5        | 21  | 131            | 79                     | 42               | 54               | 0.78    |

<sup>a</sup> Total amount of branches determined by <sup>1</sup>H NMR.

<sup>b</sup> Fraction of 1,2-insertions determined by <sup>1</sup>H NMR assuming only insertions into primary alkyl – nickel bonds; %1,2-ins. = N/167  $\times$  100.

<sup>c</sup> Relative numbers of selected branches determined by <sup>13</sup>C NMR.

NMR, the lowest degree of chain rearrangement. Presence of these types of branches, usually observed with palladium catalysts [8,17], might be caused by more facile monomer insertion into less sterically hindered secondary alkyl-nickel bonds. Similar behavior was recently observed for hex-1-ene polymerization catalyzed by complexes 1 and 2, when 2,5- and 1,5-insertions of hex-1-ene were detected as a consequence of monomer insertion into the secondary alkyl-nickel bonds [22]. Semi-quantitative comparison of insertion fashions for investigated catalysts could be done calculating relative numbers of butyl and methyl branches per 1000 C atoms obtained from the ratio of butyl or methyl signals intensity to intensity of all <sup>13</sup>C NMR spectra signals. According to <sup>1</sup>H NMR data the highest degree of rearrangement (lowest %1,2-ins.) was displayed by bulky monosubstituted complex 2 which display the highest 1B1/1B4 ratio. This indicates a higher fraction of 2.1-insertions followed by chain-walking and resulting in 1.6-hex-1-ene enchainment. Energetically less favorable 2.1-insertion is probably facilitated by more open geometry of complex 2. On contrary much lower chain straightening is observed for bulky disubstituted complex 1 that produced polyhexene with 127 branches/1000 C atoms and, according to <sup>13</sup>C NMR, high amount of monomer was inserted regularly in 1,2-fashion leading to butyl branches. Less bulky complexes **4** and **5** afforded polyhexene with approximately same degree of chain rearrangement and similar ratio of methyl to butyl branches.

Obviously, the changes of branching influence the thermal properties of polymer. The DSC traces of poly(hex-1-ene)s with approximately the same molar mass and different branching are shown in Fig. 8.

Samples with a higher degree of branching are completely amorphous and only glass transition could be observed (Fig. 7, run 16). Performing the hex-1-ene polymerization with a bulky catalyst like **2**, poly(hex-1-ene) with significantly rearranged monomer units is produced leading to the formation of linear "polyethylene-



Fig. 8. DSC traces of poly(hex-1-ene)s with 146 branches/1000 C atoms (run 16), 109 branches/1000 C atoms (run 7) and 100 branches/1000 C atoms (run 25).

like" domains long enough to crystallize which is reflected by appearance of the broad melting endotherm in DSC trace beside the glass transition (run 7). The same behavior is observed when the polymerization is carried out with a less bulky catalyst under reaction conditions favorable for chain-walking, i.e. at a higher temperature and a lower monomer concentration (run 25).

#### 4. Conclusions

Benchmark investigation of olefin polymerization catalyzed by five basic nickel diimine complexes with different substituents in ortho aryl positions was performed in order to assess the degree of their livingness/controllability. The reaction condition range within which polyolefins having narrow molar mass distribution could be prepared was expanded to higher temperatures and higher monomer/initiator ratios for selected catalysts, allowing one to prepare polyolefins with molar masses  $10^3$  to  $10^5 \,\mathrm{g \, mol^{-1}}$  and dispersity below 1.15. Despite the evidence of the presence of the side reactions, even complexes **3** and **4** with methyl groups in ortho positions of diimine ligand can be used for the preparation of polyolefins with controlled molar mass and low dispersity. The control of polymerization was demonstrated by linear evolution of molar mass on polymer conversion for complexes 4 and 5 with methyl and ethyl ortho substituents. According to all examinations performed, the complex 5 bearing ethyl groups shows almost perfect living polymerization behavior in hex-1-ene as well as propene polymerizations (beside previously reported and well documented living polymerization of complexes 1 a 2) and is a good candidate for e.g. preparation of block olefin copolymers. In addition, kinetic investigations confirmed a negligible extent of transfer and termination reactions at low temperatures for the most of catalysts. By choice of the catalyst, monomer and reaction conditions, polymer microstructure could effectively be varied in a large extent simultaneously with control over polymer molar mass.

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## Living/controlled hex-1-ene polymerization initiated by nickel diimine complexes activated by non-MAO cocatalysts: Kinetic and UV-vis study

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ABSTRACT

their absorption spectra was suggested.

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#### 1. Introduction

Polyolefins represent the largest commodity plastics group. It is due to their structural and consequently properties versatility [1]. One of the further developments in a new polyolefin materials preparation is represented by macromolecular engineering [2] and its methods: living/controlled coordination polymerization [3] and chain-shuttling [4]. Despite the lower productivity of living/ controlled olefin polymerization (one chain per growing center) in comparison with chain-shuttling, it is the most precise method of macromolecule construction.

One of the interesting post-metallocene catalyst groups allowing living/controlled polymerization of olefins [5] is represented by diimine late metal complexes [6,7]. Especially nickel derivatives are of current interest due to their high polymerization activity toward both ethylene and higher olefins. The lack of the stereospecificity control of these catalysts is balanced by their inconvenient mechanistic feature, so called chain-walking mechanism, allowing the catalytic center to migrate back into the growing polymer chain [6,8]. Chain-walking thus allows one to form branching points in the polymer arising from ethylene homopolymerization or to straighten the incorporated monomer unites in higher olefin polymerization  $(1,\omega$ -insertion). In both cases the polyolefin materials ranging from

completely amorphous (rubbery) to semi-crystalline can be prepared [9].

Living/controlled polymerization of hex-1-ene initiated by nickel diimine catalysts of general form [ArN=C

(1,8-naphthalenediyl)C=NAr]NiBr<sub>2</sub> activated by simple organoaluminium compounds was investigated.

Polyhexenes with a very narrow molar mass distribution and molar mass controlled by the monomer/initi-

ator ratio were prepared using diethylaluminiumchloride, ethylaluminiumdichloride and methyl-

aluminium dichloride as cocatalysts for nickel complexes 1 (Ar = 2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and 2 (Ar = 2-tBuC<sub>6</sub>H<sub>4</sub>). Nickel

complexes with smaller aryl substituents (3, Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; 4 Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; 5, Ar = 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)

undergo transfer reactions significantly. For the most bulky complex 1 activated by ethylaluminiumdichloride

living hex-1-ene polymerization was achieved, proved by the reinitiation of polymer growth upon the addition of fresh monomer. The effect of Al/Ni ratio on the activity of the catalytic systems was studied by

dilatometry. The catalytic systems were investigated by UV-vis spectrometry and a new interpretation of

Most of the catalytic systems are bicomponent, formed by the activation of a catalyst precursor (catalyst, initiator) by a cocatalyst (activator). The most common cocatalysts for homogeneous olefin polymerization catalysts are methylalumoxane (MAO), borates, boranes and less often simple organoaluminium compounds  $(AIR_nX_{3-n}, X = halogen atom)$  [10]. MAO is the most widely used cocatalyst for nickel diimine catalysts and, in comparison with metallocenes, 10-100 times less of it is sufficient to activate nickel complexes (Al/Ni =  $10^1$ – $10^2$ ) [11]. Compared to other catalytic systems allowing living/controlled olefin polymerization, nickel diimine complexes can be activated directly by commercially available MAO which contains around 30% of trimethylaluminium (TMA) that usually acts as a chain transfer agent and must be removed before contact with a catalyst [12-14]. However, MAO has several drawbacks. Beside the fact that its structure is not perfectly known, MAO is instable and its activation ability decreases during the storage. Safety and economic reasons for its more complicated manufacture in comparison with simple organoaluminium compounds should also be considered.

In contrast to early transition metal based catalysts that are predominantly activated by MAO, nickel diimine catalysts can be activated also by simple organoaluminiums which usually fail in an activator role for the most of metallocene catalysts [15-21]. Moreover, much lower Al/Ni ratios (Al/Ni  $= 10^{0}$ ) were shown to be

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sufficient for activation of nickel diimine complexes in ethylene polymerization when using simple organoaluminium compounds instead of MAO [22,23]. Coates et al. used diethylaluminiumchloride (DEAC) to activate Ni complexes **1** and rac-[ArN=C(1,8-naph-thalenediyl)C=NAr]NiBr<sub>2</sub>, Ar=(2-(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)ethyl-4-methyl) C<sub>6</sub>H<sub>3</sub>] to polymerize hex-1-ene, hept-1-ene and oct-1-ene to polymers with very narrow molar mass distribution ( $\mathcal{D} = 1.06-1.15$ ) at -40 °C to maximize selectivity for  $\omega$ ,2-enchainment [24].

During the investigation of living olefin polymerization Peruch and we found that the activation of nickel complexes by MAO is not quantitative and up to 30% of catalyst is converted into inactive species [11,25]. This behavior was correlated with UV–vis spectra of the catalytic system by Peruch et al. [11]. Species with absorption around 530 nm were ascribed to active species and band at 710 nm was proposed to be caused by inactive species with unknown structure. Interpretation of the spectra was based on the observation that the increase of peak at 710 nm and decrease of peak at 530 nm at room temperature is accompanied with the lost of catalyst livingness. Also the other UV–vis investigations of nickel diimine catalytic systems explained a similar observation by equilibrium between active and inactive (dormant) species [26–28].

Here, we describe several new catalytic systems based on non-MAO cocatalysts and nickel diimine complexes that enable living/ controlled olefin polymerization. Kinetics and UV–vis spectral behavior of non-MAO based catalytic systems were investigated and a new interpretation of catalyst absorption spectra was proposed.

#### 2. Experimental part

All manipulations with air-sensitive compounds were done using standard Schlenk techniques. Nitrogen (SIAD, 99.999%) was purified by passing through a column packed with Cu-catalyst and molecular sieves to remove traces of oxygen and water. Chlorobenzene (p.a., Penta) was refluxed over CaH<sub>2</sub> and distilled under nitrogen. Hex-1-ene (99%, Aldrich) was dried over sodium/potassium alloy and distilled under nitrogen. MAO (10 wt% solution in toluene, Aldrich), diethylaluminiumchloride (1.8 M in toluene, Aldrich), ethylaluminiumchloride (EADC, 1.0 M in hexanes, Aldrich), dimethylaluminiumchloride (DMAC, 1.0 M in hexanes, Aldrich), methylaluminiumdichloride (MADC, 1.0 M in hexanes, Aldrich) were used as received. Nickel complexes were synthesized and purified according to reported procedures [7,17].

Polymerizations were carried out under dry nitrogen in magnetically stirred 20 mL glass ampoules. Ampoules with chlorobenzene, hex-1-ene and initiator were placed in a bath kept at a desired temperature and tempered for 15 min. Polymerization was initiated by addition of the cocatalyst solution (MAO, DEAC, EADC, DMAC or MADC). After the desired reaction time the polymerization was quenched by 1 mL of 10% HCl in MeOH, polymer was precipitated in 300 mL of MeOH, washed by MeOH and dried at 50 °C under vacuum until constant weight. Kinetics of hex-1-ene polymerization was followed in 10 mL capillary dilatometer equipped with a PTFE valve. Monomer conversion (Y) was calculated according to eq. (1):

$$Y = \frac{L_0 - L_t}{(L_0 - L_{\text{term}}/Y_{\text{w}})}$$
(1)

where  $L_0$  is the level of polymerization mixture at the moment of activation,  $L_t$  is level at time t,  $L_{term}$  is the level at the moment of termination and  $Y_w$  is gravimetrical conversion of monomer calculated from the ratio of mass of the obtained polymer to the mass of monomer. Apparent propagation rate constants and initial propagation rates of the polymerization were calculated from the following expressions (2) and (3):

$$\ln([M_0]/[M]) = \ln(1/(1-Y)) = k_p^{app} \times t$$
(2)

$$R_{\rm p} = k_{\rm p} \times [\rm Ni]^{\alpha} [\rm Al]^{\beta} [\rm M]^{\gamma} = k_{\rm p}^{\rm app} \times [\rm M]^{1} \tag{3}$$

where [M<sub>0</sub>]and [M] are the initial and instantaneous concentration of monomer;  $\alpha$ ,  $\beta$  and  $\gamma$  are the kinetic orders with respect to Ni catalyst, Al cocatalyst and hex-1-ene monomer, respectively. As the first-order time-conversion plots were linear at least up to 50% conversion, initial rates of polymerizations were calculated using  $\gamma = 1$ , assuming first order to monomer kinetics.

UV-vis spectra of catalytic systems were recorded on a Varian Cary 50 spectrometer. A quartz cell (0.5 cm optical length) connected directly to a Schlenk flask was used for measurements.

The microstructure of polyhexenes was determined by  $^{1}$ H NMR spectroscopy on 500 MHz Bruker Avance DRX 500 spectrometer in CDCl<sub>3</sub> solution at 30 °C.

The total number of branches per 1000 carbon atoms (N) was determined by integrating methyl proton signals with respect to signals of all protons in <sup>1</sup>H NMR spectrum and calculated using the formula:

$$N = \frac{2(I_{CH_3})}{3(I_{CH+CH_2+CH_3})} \times 1000$$
(4)

The degree of polyhexene chain rearrangement (x) expressed as the fraction of 1,6-monomer insertions was calculated according to expression (5):

$$x = \left(1 - \frac{N}{167}\right) \times 100(\%) \tag{5}$$

Molar masses were determined using Waters Breeze chromatographic system equipped with RI detector operating at 880 nm and multi-angle laser light scattering (MALLS) miniDawn TREOS from Wyatt operating at 658 nm. Separations were performed with two Polymer Laboratories Mixed C columns at 35 °C in THF at an elution rate of 1 mL min<sup>-1</sup>. The dn/dc value 0.078  $\pm$  0.002 mL g<sup>-1</sup> was used for polyhexene in THF at 35 °C [29].

#### 3. Results and discussion

#### 3.1. Controlled polymerization

To study the behavior of catalytic systems activated by non-MAO catalysts, five nickel catalysts were used that are known to initiate living/controlled olefin polymerization when activated by MAO (Fig. 1) [29]. First, bulky t-butyl substituted catalyst **2** was used in the polymerization of hex-1-ene for screening of four simple organoaluminium compounds: diethylaluminiumchloride (DEAC),



Fig. 1. Structure of nickel diimine complexes used in this work.

 Table 1

 Polymerization of hex-1-ene initiated by complex 2 activated with various cocatalysts.

| Run | Cocatalyst | Monomer<br>conversion [%] | $M_n^a$ kg·mol <sup>-1</sup> | Ða  | NPM/N(Ni) <sup>b</sup> | N <sup>c</sup> |
|-----|------------|---------------------------|------------------------------|-----|------------------------|----------------|
| 1   | MAO        | 100                       | 84.2                         | 1.3 | 0.8                    | 93             |
| 2   | DEAC       | 100                       | 57.7                         | 1.3 | 1.2                    | 73             |
| 3   | EADC       | 100                       | 74.3                         | 1.4 | 0.9                    | 67             |
| 4   | DMAC       | 85                        | 11.5                         | 2.2 | _                      | 64             |
| 5   | MADC       | 70                        | 60.5                         | 1.3 | 0.8                    | 80             |

[Ni] = 1.0 mM, Al/Ni = 500, [hex-1-ene] = 0.8 M, chlorobenzene, total volume 10 mL,  $T_p = 0$  °C, time of polymerization 4 h.

<sup>a</sup> Number average molar mass and dispersity determined by SEC with PS standards.

<sup>b</sup> NPM/N(Ni) = polymer mass/(mol<sub>Ni</sub>·M<sub>n</sub>).

<sup>c</sup> Number of branches per 1000 C atoms determined by <sup>1</sup>H NMR spectroscopy.

ethylaluminiumdichloride (EADC), dimethylaluminiumchloride (DMAC) and methylaluminiumdichloride (MADC) in role of cocatalysts (activators) and compared with MAO (Table 1). Compared to methyl aluminium derivatives, ethyl aluminium analogues afforded more active catalytic species, completely transforming monomer into polymer in 4 h at 0 °C. With the exception of DMAC, all catalytic systems produced polyhexene with narrow molar mass distribution, comparable to that of the polyhexene produced by MAO activated catalyst, suggesting controlled polymerization with respect to molar mass. Efficiency of the catalysts was further expressed by number of polymer molecules produced per molecule of initiator [NPM/N(Ni)] calculated from the amount of obtained polymer, amount of Ni catalyst and molar mass of polymer. For all the catalytic systems producing polymers with low dispersity, NPM/N(Ni) is closed to unity showing a good efficiency of simple organoaluminium compounds as the activators of nickel complex 2 and further showing that molar masses of the prepared polymers are appropriate to monomer/initiator ratio, another typical feature of living/controlled polymerizations.

Concerning the microstructure of the polymers we found that the choice of cocatalyst influences also the branching of the polymer chain in agreement with previous studies of ethylene and propylene polymerization [15,17,20]. All polymerizations activated by simple organoaluminium compounds led to polyhexene with lower amount of branches than in MAO activated system, which shows higher degree of chain-walking reactions in comparison to propagation. The highest degree of rearrangement (62%) was observed for DMAC. Comparison with MAO activated catalyst (44% rearrangement) indicates the possibility to efficiently control the polymer microstructure also by choice of the cocatalyst.

Since some chain transfer was evident from slightly broadened molar mass distribution of the polyhexenes prepared at 0 °C, further experiments were carried out at -10 °C to minimize the extent of side reactions. Other four nickel complexes were tested in combination with the most effective cocatalysts DEAC and EADC. Based on the kinetic investigation (see below) and literature data for 2/MAO [11], which show reaching activity plateau at Al/Ni = 50, we used decreased Al/Ni = 200 ratio for the rest of experiments. As seen from Table 2, all the catalysts activated by MAO gave high yield of polyhexene with a very low dispersity in molar masses in agreement with previously published works [7,29]. Using DEAC or EADC, only bulky catalysts 1 and 2 produced polyhexenes with a narrow molar mass distribution at high yield, indicating a controlled manner of the polymerization. NPM/N(Ni) values within these two nickel complexes are very close to unity using DEAC and EADC as cocatalysts supporting further a controlled character of the polymerization.

In the case of complexes **3** and **4** with methyl ortho-substituents, significantly broadened molar mass distribution was observed and, using EADC, also the catalyst activity dropped substantially.

Table 2

Polymerization of hex-1-ene initiated by **1–5** activated by MAO, DEAC and EADC in chlorobenzene.

| Run | Catalyst | Cocatalyst | Yw <sup>a</sup><br>[%] | Mn <sup>b</sup><br>[kg.mol <sup>-1</sup> ] | Ðb   | NPM/N(Ni) <sup>c</sup> | N <sup>d</sup> |
|-----|----------|------------|------------------------|--|------|------------------------|----------------|
| 1   | 1        | MAO        | 89                     | 91.6                                       | 1.03 | 0.70                   | 127            |
| 2   |          | DEAC       | 94                     | 59.3                                       | 1.07 | 1.08                   | 113            |
| 3   |          | EADC       | 88                     | 58.3                                       | 1.11 | 1.05                   | 118            |
|     |          |            |                        |  |      |                        |                |
| 4   | 2        | MAO        | 95                     | 60.8                                       | 1.13 | 1.11                   |                |
| 5   |          | DEAC       | 84                     | 48.9                                       | 1.27 | 1.11                   |                |
|     |          |            |                        |  |      |                        |                |
| 6   | 3        | MAO        | 90                     | 59.1                                       | 1.30 | 1.09                   |                |
| 7   |          | DEAC       | 94                     | 39.6                                       | 1.97 | _                      |                |
| 8   |          | EADC       | 30                     | 89.7                                       | 1.67 | _                      |                |
|     |          |            |                        |  |      |                        |                |
| 9   | 4        | MAO        | 75                     | 60.1                                       | 1.13 | 0.85                   |                |
| 10  |          | DEAC       | 66                     | 20.2                                       | 2.71 | _                      |                |
| 11  |          | EADC       | 4                      | 33.7                                       | 2.13 | _                      |                |
|     |          |            |                        |  |      |                        |                |
| 12  | 5        | MAO        | 90                     | 66.0                                       | 1.08 | 1.09                   | 131            |
| 13  |          | DEAC       | 95                     | 49.7                                       | 1.30 | 1.33                   | 115            |
| 14  |          | EADC       | 50                     | 74.7                                       | 1.41 | 0.46                   | 124            |
|     |          |            |                        |  |      |                        |                |

[Ni] = 1.0 mM, Al/Ni = 200, [hex-1-ene] = 0.8 M, polymerization time 5 h,  $T_{\rm p} = -10~^\circ{\rm C}$ , total volume 10 mL.

<sup>a</sup> Monomer conversion.

<sup>b</sup> Number average molar mass  $(M_n)$  and dispersity determined by SEC-MALLS.

<sup>c</sup> NPM/N(Ni) = polymer mass/(mol<sub>Ni</sub>· $M_n$ ).

<sup>d</sup> Number of branches per 1000 C atoms determined by <sup>1</sup>H NMR spectroscopy.

Complex **5** with ethyl substituents was efficiently activated only by DEAC producing polyhexene with fairly low dispersity values. However, when activated by EADC, complex **5** showed only low monomer conversion and, according to NPM/N(Ni) parameter, less than half of the nickel precursor was activated. This is in contrast with our previous experiments in which MAO activated complex **5** controlled hex-1-ene polymerization in a similar or even better manner than the most widely used complex **1** [29]. This stress out the role of MAO as a bulky cocatalyst which helps to protect the Ni center from  $\beta$ -eliminations and ensures the livingness of polymerization even in case of less bulky Ni diimine complexes.

At -10 °C, chain walking is less pronounced [6,30] and polyhexenes with a similar branching degree are obtained with catalysts **1** and **5**. DEAC and EADC again showed higher degree of rearrangement in comparison with MAO leading to less branched polymers in case of both catalysts.

The best control over the polymerization activated by DEAC and EADC was achieved with bulky catalyst **1** demonstrated by a very



**Fig. 2.** SEC traces of polyhexenes obtained by nickel complex **1** activated by MAO (dash dot), EADC (solid) and DEAC (dash). [Ni] = 1.0 mM, Al/Ni = 200, [hex-1-ene] = 0.8 M, 5 h,  $T_p = -10$  °C



**Fig. 3.** SEC chromatograms of polyhexenes obtained by nickel complex **1** activated by EADC after 5 h of polymerization (right peak) and after reinitiation by addition of second portion of monomer after additional 12 h of polymerization (left peak).  $T_p = -10$  °C, [Ni] = 1.0 mM, Al/Ni = 200, [hex-1-ene] = 0.4M + 0.4 M. Monomer conversion 96%.

narrow molar mass distribution, similar to that obtained by 1/MAO (Fig. 2). To investigate the livingness of these catalytic systems we decided to perform a reinitiation experiment consisting of the addition of fresh monomer after the consumption of initial



**Fig. 4.** First-order time-conversion plots of hex-1-ene polymerization initiated **2**/DEAC (A) and **2**/EADC (B),  $T_p = -10$  °C, [Ni] = 1.0 mM, [hex-1-ene] = 0.8 M; 1 < Al/Ni < 200.

Table 3

Influence of Al/Ni ratio on hex-1-ene polymerization initiated by  $\mathbf{2}/\text{EADC}$  in chlorobenzene.

| Run | Al/Ni | Yw <sup>a</sup><br>% | M <sub>n</sub> <sup>b</sup><br>kg mol <sup>−1</sup> | $D^{\mathrm{b}}$ | NPM/N(Ni) <sup>c</sup> |
|-----|-------|----------------------|---|------------------|------------------------|
| 1   | 200   | 89                   | 52.8  | 1.14             | 1.13                   |
| 2   | 100   | 85                   | 53.7  | 1.23             | 1.05                   |
| 3   | 50    | 87                   | 59.7  | 1.22             | 0.97                   |
| 4   | 20    | 86                   | 72.8  | 1.07             | 0.78                   |
| 5   | 10    | 85                   | 62.0  | 1.15             | 0.91                   |
| 6   | 5     | 82                   | 67.7  | 1.07             | 0.81                   |

[Ni] = 1.0 mM, [hex-1-ene] = 0.8 M, polymerization time 4 h,  $T_{\rm p}$  = -10 °C, total volume 10 mL.

<sup>a</sup> Monomer conversion.

 $^{\rm b}$  Number average molar mass ( $M_{\rm n}$ ) and dispersity determined by SEC-MALLS.

<sup>c</sup> NPM/N(Ni) = polymer mass/(mol<sub>Ni</sub>· $M_n$ ).

monomer feed. Although 1/DEAC produced polyhexene with narrower molar mass distribution than 1/EADC, DEAC activated system failed in the reinitiation test and, according to SEC traces, significant portion of growing centers was inactive in the second phase of polymerization. On contrary, 1/EADC system surprisingly displayed very good reinitiation capability, polyhexene molar mass was doubled (and equaled to theoretical value) and its distribution remained very narrow after second monomer addition (Fig. 3). This could be explained by the coordination of activator molecule to Ni center after complete monomer consumption, which is stronger in case of DEAC compared to EADC (vide infra).

#### 3.2. Kinetics of polymerization

To investigate the reactivity of catalytic systems toward olefin, kinetic measurements were carried out by means of dilatometry. For this purpose we used nickel complex **2** activated by DEAC and EADC and compared with MAO. All experiments with MAO and DEAC displayed first-order kinetics with respect to hex-1-ene concentration in the initial period of polymerization. Typical first-order kinetic plots for **2**/DEAC system are shown in Fig. 4A. At Al/Ni ratio lower than five, polymerization did not proceed up to high conversion due to the consumption of significant part of cocatalyst by impurities. In the case of **2**/EADC system an induction period, shortening with increase of Al/Ni ratio, was observed caused by



**Fig. 5.** Logarithmic variations of hex-1-ene polymerization rate on activator concentration, in chlorobenzene at -10 °C, complex **2**. [Ni] = 1.0 mM, [hex-1-ene] = 0.8 M; 0.0009 < [Al] < 0.1966 M; 1 < Al/Ni < 200. Cocatalysts: MAO (diamonds), DEAC (squares), EADC (triangles).



**Fig. 6.** UV–vis spectra of **2**/DEAC catalytic system activated in presence of hex-1-ene: after activation (curve 1), after 8 h of polymerization (curve 2), after addition of second portion of hex-1-ene (curve 3). [hex-1-ene] = 0.4M + 0.4 M, [Ni] = 0.8 mM, Al/Ni = 200,  $T_p = 0$  °C.

slow activation (Fig. 4B). Once activated all centers propagate at a similar rate and the polymerization follows first-order kinetics to monomer as in the case of DEAC and MAO activation. Propagation constants were therefore calculated from the linear part of  $ln([M]_0/[M])$  dependence on polymerization time to allow the comparison with the other systems using the same kinetic model. Despite relatively slow activation rate of EADC, polyhexenes with a very low dispersity were prepared even at low Al/Ni ratios as a consequence of rather slower propagation (Table 3). However, the decrease of Al/Ni ratio leads to the detectable decrease of polymerization activity as a consequence of lower initiator efficiency caused by incomplete activation of complex **2** by EADC at Al/Ni ratios below 50, as visible from decrease of NPM/N(Ni) values.

Initial propagation rates of hex-1-ene polymerization were calculated and plotted against Al/Ni ratio (Fig. 5). In case of all the activators, an increase of activity with increase of Al/Ni ratio was observed followed by reaching a plateau. This breakpoint was reached at Al/Ni = 50 for MAO, which is in exact agreement with the previous work of Peruch [11]. For DEAC and EADC the activity plateau was reached at considerably lower Al/Ni ratio equal five. From this point of view, DEAC and EADC seem to be more efficient cocatalysts. According to maximum activity values DEAC forms the most active catalytic system with complex **2** in comparison to EADC and MAO which displayed similar propagation rate.

#### 3.3. UV-vis spectroscopy of catalytic systems

In previously published literature [11], UV–vis spectroscopy was suggested as a method for investigation of catalytic species obtained by MAO activated catalyst **2**. Two characteristic peaks in **2**/MAO UV–vis spectra were ascribed to two types of species: active,



**Fig. 7.** UV–vis spectra of **2**/DEAC catalytic system activated in absence of hex-1-ene (curve 1), in presence of hex-1-ene (curve 2-after monomer addition, curve 3-after 18 h).[hex-1-ene] = 0.4 M, [Ni] = 0.8 mM, Al/Ni = 200,  $T_p = -10$  °C.

absorbing at 530 nm, and inactive, absorbing at 700 nm. The stability of the absorption spectra at -10 °C was correlated with the stability of active centers and therefore with livingness of the catalytic system. At room temperature authors observed the evolution of spectra when peak at 530 nm (active species) decreased while simultaneously peak at 700 nm increased its intensity which was accompanied by the lost of livingness.

In our UV–vis experiments we observed much different behavior of non-MAO activated nickel complexes. In contrast to MAO activated system both DEAC and EADC activated complex **2** displayed only one peak at 530 nm in UV–vis spectra from 400 to 900 nm (Fig. 6, curve 1).

Assuming the active-inactive species hypothesis it would mean that only active species were formed and nickel complexes were quantitatively activated. NPM/N(Ni) values for bulky catalysts 1 and 2 were close to unity (Tables 1 and 2) which would support the idea of complete catalyst activation. However, in the case of 2/DEAC activated system, we observed the formation of a new peak around 650 nm at prolonged reaction times (after 8 h at 0 °C), when the conversion of monomer is completed (Fig. 6, curve 2). Simultaneously, the peak at 530 nm disappeared and the mixture color turned from violet to green. At this moment we added fresh hex-1-ene to the mixture. To our surprise, we observed that the apparently inactive catalytic system reacted with the monomer leading to the disappearance of the peak at 650 nm and regeneration of the peak at 530 nm (Fig. 6, curve 3). Simultaneously, the color of the mixture turned to red immediately after monomer addition and increased its intensity returning back to deep violet color in several hours. Such easily observable changes in color mixture could be useful for indication of monomer consumption which could be advantageous e.g. in preparation of block copolymers by sequential monomer addition.



X=solvent or activator molecule



**Fig. 8.** UV-vis spectra of **1**/MAO catalytic system activated in presence of hex-1-ene (curve 1), after addition of styrene (curve 2) and after addition of methylacrylate (curve 3). [hex-1-ene] = 0.4 M, [Ni] = 0.8 mM, Al/Ni = 200,  $T_p = -10$  °C, styrene/Ni = 10, methylacrylate/Ni = 10.

However, intensity of the peak at 530 nm did not reach the initial value of freshly activated system indicating some decomposition of the catalytic system in absence of monomer. This instability of nickel diimine catalyst was observed previously for MAO activated system [11]. Despite some catalyst deactivation the most of the monomer from both feeds was converted to polymer (conversion 91%). However, SEC analysis of the sample withdrawn from the polymer mixture before second monomer addition and after it revealed a substantial increase of molar mass dispersity as a consequence of termination of chain growth on deactivated centers.

The above described behavior of the catalytic system led us to a proposal of new explanation of the absorption spectra in which peak at 530 nm corresponds to alkyl-olefin Ni complex (Scheme 1, structure **A**), known as the resting state (active species) of diimine catalysts [5,9,30], whereas the peak at 650 nm do not belong to inactive centers but corresponds to alkyl-Ni complex with "vacant" coordination position (Scheme 1) which can be converted back to complex **A** by the addition of fresh monomer. It is probable that hypothetical complex with free coordination position would be instable in the reaction mixture and would immediately coordinate either solvent or rather cocatalyst molecule. Therefore, species absorbing at 650 nm could be described more properly as complex **B** (Scheme 1) with coordinated solvent or cocatalyst molecule, which could be replaced by strongly binding olefin molecule to regenerate the active complex **A**. The interaction between Ni center and activator halogen atom (Ni…Cl–Al) was already proposed and investigated by several X-ray absorption methods by de Souza et al. [31].

To support our hypothesis, we performed an additional experiment in which complex 2 was activated by DEAC in absence of hex-1-ene. UV-vis spectra (Fig. 7, curve 1) displayed only one peak at 650 nm. Addition of hex-1-ene to the mixture leads to immediate disappearance of the peak at 650 nm and formation of the intensive peak at 530 nm belonging to active species as a consequence of replacement of coordinated activator molecule by hex-1-ene (Fig. 7, curve 2). Complete reaction of hex-1-ene with catalyst took several hours as indicated by slow increase of intensity of the peak at 530 nm (Fig. 7, curve 3). The reaction produced polyhexene with molar mass 22 800 g mol<sup>-1</sup> and dispersity D = 2.66 after 20 h reaching conversion of only 36% suggesting partial irreversible deactivation of the catalyst centers and competition between monomer and activator coordination to Ni center. Compared to values obtained in experiments when the catalyst was activated in presence of monomer (Table 2, run 5) this observation emphasizes the importance of monomer presence at the stage of nickel catalyst activation.



R= alkyl or polymeryl X= activator or solvent molecule

Scheme 2. Proposed mechanism of active and dormant centers origin and their transformation by addition of terminating agents.

A similar behavior was observed also in EADC activated system which afforded a peak at 530 nm after the activation in presence of monomer. In absence of monomer the peak at 700 nm was formed. In comparison with DEAC, no peak at 700 nm is generated even after prolonged reaction times if nickel catalyst is activated by EADC in presence of monomer. That could be explained by the presence of small amount (1% of remaining monomer at 99% conversion is enough to coordinate all Ni centers) of unreacted monomer (or olefin generated by  $\beta$ -H elimination) which is sufficient to form alkyl-olefin complex A. The position of peak corresponding to species **B** is thus influenced by cocatalyst and for EADC and MAO have maximum at approximately 700 nm whereas for DEAC at 650 nm. The shift in maximum absorption is probably caused by different interaction of Ni complex cation and counteranion generated from each cocatalyst or by coordination of cocatalyst molecules to vacant position of nickel complex after monomer consumption.

This interaction is important for spectral behavior of the catalytic system, because the addition of hex-1-ene to MAO activated system does not lead to diminution of the peak at 700 nm and even the spectra obtained in presence of monomer at low temperatures, when the system is living, contain the peak at 700 nm [11]. This could be explained by the stabilization of alkyl nickel complex **B** by bulky MAO counteranion (we excluded the coordination of trimethylaluminium present in MAO by using dried MAO in another experiment) which, in absence of monomer, can coordinate to nickel complex and block the coordination of monomer to part of nickel centers. Therefore, we decided to investigate MAO activated catalytic system in more detail to prove the consistency of our mechanistic explanation. For this purpose we reacted MAO activated system with compounds that coordinate to nickel center stronger than hex-1-ene. In Fig. 8, curve 1 represents MAO activated complex **1** in presence of hex-1-ene at -10 °C when the catalyst is considered to be stable. Two main peaks at 530 nm and 700 nm were observed as in previous studies and that we propose to be alkyl-olefin complex A and alkyl complex B with coordinated activator (Scheme 2). Addition of styrene led to the shift of the peak at 530 nm to 580 nm confirming the replacement of hex-1-ene by strongly coordinating styrene (Fig. 8, curve 2). However, the peak at 700 nm remained unchanged indicating that styrene was not capable to coordinate strong enough to break the interaction between cationic center and MAO. Therefore, we added methylacrylate, which due to its polar group coordinate stronger than non-polar olefins, and we observed immediate disappearance of the peak at 700 nm and increase of intensity of the peak at 580 nm (Fig. 8, curve 3). This shows that the peak at 700 nm represents species that are capable of further coordination and could be represented by alkyl complex **B** in which the vacant position is blocked by MAO.

#### 4. Conclusions

We found that controlled polymerization of olefins can be initiated by bulky nickel diimine complexes **1** and **2** activated by non-MAO cocatalysts resulting in polyolefins with a very narrow molar mass distribution and molar mass tunable by monomer/ initiator ratio. EADC activated catalyst **1** displayed truly living behavior enabling reinitiation of chain growth after fresh monomer addition. Kinetics investigation shows that simple organoaluminium compounds are efficient cocatalysts at order of magnitude lower Al/Ni ratios in comparison with MAO while the polymerization remains controlled. Despite slower activation, EADC activated catalytic systems afford polyhexenes with a narrow molar mass distribution. We proposed a new interpretation of UV–vis spectra of the catalytic systems based on partially reversible conversion between alkyl-olefin Ni (**A**) and alkyl-Ni complexes with coordinated activator (**B**). The hypothesis was supported by changes of spectra during the polymerization and upon addition of monomer or terminating agents.

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Ρ5

# Organic support for ethylene polymerization based on the self-assembly in heptane of end-functionalized polyisoprene

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In this work, we report how micellar structures obtained by the self-assembly in heptane of polyisoprene end-capped with a hindered tertiary alcohol moiety (PI- $\varphi_2$ OH) can be efficiently used as organic supports for olefin polymerization single-site catalysts. PI- $\varphi_2$ OH has been synthesized by end-capping living polyisoprenyllithium with an excess of benzophenone. Dynamic light scattering analysis indicates a self-assembly of PI- $\varphi_2$ OH in heptane, a good solvent for polyisoprene and a poor one for the polar end-group. The so-formed micelle-like nanoparticles, composed of a di-phenyl alcohol group core and a polyisoprene corona were used as organic supports for catalytic system composed of aluminic activators, trimethylaluminium (TMA) or methylaluminoxane (MAO), and metallocene or post-metallocene catalysts, to produce micrometric polyethylene beads.

## Introduction

Metallocenes and late transition metal complexes are effective catalysts for the homogeneous polymerization of olefins, enabling the production of polyolefins with a tunable microstructure and molecular weight distribution. In order to control the polyolefin morphology (formation of beads) and also to prevent fouling of large scale reactors in industry, fixing the catalytic system on a support is required. The immobilization of catalytic systems is generally performed with a solid inorganic carrier<sup>1,2</sup> such as silica,<sup>3</sup> alumina<sup>4</sup> and magnesium chloride.<sup>5,6</sup> After polymerization, some residual inorganic support can remain in the polyolefin which affects the optical and mechanical properties of the final materials.<sup>7,8</sup> To avoid such a drawback, one solution is to replace the inorganic supports with organic templates. Most of the investigations carried out have been on the development of functional organic supports essentially based on polystyrene (PS).<sup>9</sup> For instance, a metallocene catalyst can be attached to a PS backbone through its aromatic ligands.<sup>10-13</sup> Another strategy is to anchor the activator, generally methylaluminoxane (MAO) or trimethylaluminium (TMA), on a polar organic support thanks to weak oxygen-aluminium interactions. Typically, PS nanogel with a small number of peripheral ethylene oxide units was described as carrier for MAO/2,6-bis{1-2,6}-(diisopropylphenyl)imino]ethylpyridynyl iron dichloride, [MeD-IP(2,6-iPrPh)<sub>2</sub>FeCl<sub>2</sub>], a catalytic system towards ethylene polymerization.<sup>14</sup> However in all cases, a multistep synthesis of these organic templates is required that can be seen as a limitation for the industrialization.

A more straightforward strategy to design organic support is based on the self-assembly of end-functionalized polymers or

<sup>c</sup>Institute of Chemical Technology, Prague, Department of Polymers, Technická 5, 166 28 Prague 6, Czech Republic block-copolymers.<sup>15</sup> Bouilhac *et al.* have synthesized linear PS end-functionalized by a benzoic acid or a benzophenone moiety<sup>16</sup> and investigated the self-assembly in toluene of these functional PS into micellar aggregates. The purpose was the encapsulation of Fe-based catalytic system to produce millimetric polyethylene (PE) beads with a high catalytic activity. Similarly, polystyrene-*block*-poly(4-vinyl benzoic acid) copolymers were synthesized and their ability to control the PE morphology was also proven.<sup>17</sup> This new concept of support for the production of PE beads has been essentially applied on the self-assembly, in toluene, of PS-based supports with MeDIP(2,6-*i*PrPh)<sub>2</sub>FeCl<sub>2</sub> as a catalyst.

Following this strategy, we describe in this paper the use of micellar structures based on the self-assembly in heptane of polyisoprene end-capped with a diphenyl-tertiary-alcohol moiety, as nanoreactors for the production of polyolefin beads. Diphenyl-tertiary-alcohol end-group has been chosen for its polarity which induces micellization in aliphatic solvent and also for the capacity of tertiary alcohol to entrap free TMA leading to an increase of the catalytic activity.<sup>18</sup> MeDIP(2,6-*i*PrPh)<sub>2</sub>FeCl<sub>2</sub>, N,N'-bis(2,6-diethylphenyl)-2,3-(naphthalene-1,8-diyl)-1,4-diazabuta-1,3-diene) nickel(II) dibromide, [( $\alpha$ -diimine)nickel(II)] and bis(indenyl)zirconium dichloride



MeDIP(2,6-iPrPh)<sub>2</sub>FeCl<sub>2</sub>

Scheme 1 Catalysts used with  $PI-\phi_2OH$  as support for the polymerization of ethylene.

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 $[Ind_2ZrCl_2]$  (Scheme 1), were tested as catalysts in the presence of MAO or TMA as activators.

#### **Results and discussion**

#### Synthesis of PI-Ф2OH

The anionic polymerization of styrene, ended by the addition of benzophenone to quench the active species has been reported by Quirk and colleagues.<sup>19</sup> On this basis, we performed the anionic polymerization of isoprene in cyclohexane, initiated by *s*-butyl-lithium, and quenched the reaction by adding an excess of benzophenone in order to obtain low molar mass diphenylhydroxy-terminated polyisoprene (PI- $\phi_2$ OH, see Scheme 2).

As illustrated in Table 1, anionic polymerization in apolar solvent leads to a very good control over the polymer dimensions together with the advantage of working above room temperature.

The chain-end funtionnalization has been checked by <sup>1</sup>H and <sup>13</sup>C NMR. As it can be seen in the <sup>1</sup>H NMR spectrum (Fig. 1), the apparition of peaks at 7.2 and 7.5 ppm are representative of the



Scheme 2 Synthesis of polyisoprene diphenyl alcohol, PI- $\phi_2$ OH, by anionic polymerization.

**Table 1** Synthesis by anionic polymerization of  $PI-\Phi_2OH^a$ 

| Run | $M_{n,SEC}^{\ \ b}/g\ mol^{-1}$ | $D^b$ | $M_{n,NMR}^{c}/g \text{ mol}^{-1}$ | f <sup>c</sup> (%) |
|-----|---------------------------------|-------|------------------------------------|--------------------|
| 1   | 2515                            | 1.08  | 1900                               | 100                |
| 2   | 5843                            | 1.05  | 3900                               | 100                |

<sup>*a*</sup> Polymerization in cyclohexane at 50 °C. <sup>*b*</sup> Determined by SEC with THF as eluent (RI detector). <sup>*c*</sup> Determined by <sup>1</sup>H NMR.



**Fig. 1** <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of diphenyl alcohol terminated polyisoprene (run 1).

aromatic protons and the one at 3.06 ppm of the proton of the alcohol function.

## Properties of PI-Φ<sub>2</sub>OH solubilized in heptane studied by dynamic light scattering

All the PI- $\Phi_2$ OH dispersions in heptane used for the dynamic light scattering (DLS) analysis were initially heated at 65 °C and then cooled down to 30 °C to favor the micellization process. The same methodology was followed in the presence of the aluminic activator (see later in the text).

First, DLS experiments were performed on a PI- $\Phi_2$ OH ( $M_n = 2515 \text{ g mol}^{-1}$ ) dispersion at 1 mg ml<sup>-1</sup> in heptane at 30 °C.

Collected data revealed the existence of a self assembly of PI- $\Phi_2$ OH in heptane into micelle-like structures that likely consist of an alcohol core and a polyisoprene corona (heptane being a good solvent for polyisoprene). The values of the hydrodynamic radii ( $R_{\rm H}$ ) of the different nanoparticles were calculated from the decay times using the Stokes–Einstein equation. These relaxation times were determined by applying the CONTIN analysis<sup>20</sup> to the autocorrelation functions; an example is given in Fig. 2 for PI- $\Phi_2$ OH of  $M_n = 2515$  g mol<sup>-1</sup>.

The DLS analysis of higher molar mass PI- $\Phi_2$ OH ( $M_n = 5843 \text{ g mol}^{-1}$ ) in heptane at 1 mg ml<sup>-1</sup> and 30 °C showed a very low diffusion intensity indicating the presence of a main population composed of free chains (2 nm size) together with a minor second population attributed to aggregates (125 nm). This result clearly proves that such PI is not capable to form micellar structures due to a too long size of the PI chain. For this reason, lower molar mass PI- $\Phi_2$ OH ( $M_n = 2515 \text{ g mol}^{-1}$ ) was only used as template for the synthesis of PE beads.

#### Effect of MAO addition onto PI- $\Phi_2$ OH self-assembly

The effect of MAO addition onto PI- $\Phi_2$ OH self-assembly process in heptane was investigated by DLS. For this purpose, MAO was added to PI- $\Phi_2$ OH dispersion and the whole system was maintained for 24 h at 65 °C then cooled down at 30 °C. The addition of MAO (Al/OH = 75) into PI- $\Phi_2$ OH dispersion ( $M_n$  = 2515 g mol<sup>-1</sup>, c = 1 mg mL<sup>-1</sup>) leads to an increase of the particle radius (from an average value of 290 nm to 530 nm), see Fig. 3.



Fig. 2 Relaxation curve and corresponding Contin fit obtained by DLS analysis ( $\theta = 50^{\circ}$ ) of PI- $\Phi_2$ OH ( $M_n = 2515 \text{ g mol}^{-1}$ ) in heptane ( $c = 1 \text{ mg mL}^{-1}$ , T = 30 °C). The inset shows the dependency of the decay rate  $\Gamma$  on the square scattering vector  $q^2$ .



Fig. 3 Autocorrelation function and relaxation times at  $\theta = 90^{\circ}$  of PI- $\Phi_2$ OH ( $M_n = 2515 \text{ g mol}^{-1}$ ) in heptane ( $c = 1 \text{ mg ml}^{-1}$ ,  $T = 30 ^{\circ}$ C) with MAO: Al/OH = 75.

This phenomenon would indicate that some MAO is encapsulated within the aggregates.

The signal increase observed in the correlation function at high relaxation times also indicates the formation of aggregates which can be explained by the presence of non-encapsulated MAO. It is worth noting that in the absence of PI- $\Phi_2$ OH, the MAO is not dispersable in heptane at all. The encapsulation phenomenon is supported by the visual aspect of the dispersion which remains homogeneous and stable at least 2 h (no sedimentation observed). This means that MAO is fully dispersed in heptane thanks to the presence of PI- $\Phi_2$ OH.

Consequently, the decay rate *versus* squared scattering vector plot could not be fitted with a linear curve, explained by the presence of different populations of aggregates with a nonspherical shape (data not shown).

#### Effect of TMA addition onto PI- $\Phi_2$ OH self-assembly

TMA is soluble in heptane and purchased in solution (2 mol L<sup>-1</sup>) in this solvent. The effect of TMA addition (Al/OH = 25) on PI- $\Phi_2$ OH self-assembly has also been checked by DLS (see Fig. 5).



**Fig. 4** Relaxation curve and corresponding Contin fit obtained by DLS analysis ( $\theta = 50^{\circ}$ ) of PI- $\Phi_2$ OH ( $M_n = 2515$  g mol<sup>-1</sup>) in heptane ( $c = 1 \text{ mg mL}^{-1}$ ,  $T = 30 ^{\circ}$ C) with TMA: AL/OH = 25. The inset shows the decay rate  $\Gamma$  dependency to the square scattering vector  $q^2$ .

As for MAO, TMA was added to PI- $\Phi_2$ OH dispersions and the whole system was maintained for 24 h at 65 °C then cooled down at 30 °C. As expected, the addition of TMA onto PI- $\Phi_2$ OH dispersion ( $M_n = 2515$  g mol<sup>-1</sup>, c = 1 mg mL<sup>-1</sup>) leads to an increase of the particle size with a R<sub>H</sub> value of 551 nm without formation of larger aggregates as it was observed for MAO. In the case of TMA addition, the dispersion remains homogeneous and the decay rate *versus* squared scattering vector plot can be fitted with a linear curve, proof of the formation of spherical particles (inset in Fig. 4).

#### Polymerization of ethylene using MeDIP(2,6-iPrPh)<sub>2</sub>FeCl<sub>2</sub>

The micellar structures obtained from the self-assembly of PI- $\Phi_2$ OH in heptane were subsequently used to support the tridentate bis(imino) pyridinyl iron catalyst, MeDIP(2,6-*i*PrPh)<sub>2</sub>FeCl<sub>2</sub>. The polymerizations were then performed at 30 °C under 1 bar of ethylene pressure for 1 h.

The influence of the support on the production of PE using MeDIP(2,6-*i*PrPh)<sub>2</sub>FeCl<sub>2</sub> was investigated; data are collected in Table 2.

With MAO, an increase of the catalytic activity in the presence of the support compared to homogeneous conditions is observed (2987 kg PE/(mol Fe h bar, run 1, vs. 2413 kg PE/(mol Fe h bar), run blank 1). This increase can be explained by the entraping of the free TMA, present in the MAO solution, through the alcohol function of the support.

The use of TMA as a cocatalyst at a ratio Al/Fe = 500, leads to slightly higher values of catalytic activity in the presence of PI- $\Phi_2$ OH in comparison to homogeneous conditions (1753 kg PE/ (mol Fe h bar), run blank 2, *vs.* 1965 kg PE/(mol Fe h bar), run 2). This can be reasonably explained by a local increase of the cocatalyst concentration thanks to the micellar support. Reduction of Al/Fe ratio below 500 leads to a sharp decrease of the catalytic activity. According to SEC analysis, oligomers were never formed (Fig. 5), which is in agreement with a suppression/ reduction of transfer reaction to TMA, proving the efficiency of the support to trap the activator within the micelles. The



Fig. 5 SEC traces (viscosimeter) of PEs made with  $PI-\Phi_2OH$  and  $MeDIP(2,6iPrPh)_2FeCl_2$  as catalyst.

Table 2 Polymerization of ethylene in the presence of the catalytic system composed of PI- $\Phi_2$ OH + MAO or TMA and MeDIP(2,6*i*PrPh)<sub>2</sub>FeCl<sub>2</sub>

| Run                  | n(cata)/µmol | Activator | Al/Fe | Activity/kg<br>mol(C) <sup>-1</sup> h <sup>-1</sup> bar <sup>-1</sup> | Al/OH | $T_m / ^{\circ}C^c$ | χc <sup>c</sup> | $M_w^{-d}$ /kg mol <sup>-1</sup> | $D^d$   | Bead<br>size/µm |
|----------------------|--------------|-----------|-------|---|-------|---------------------|-----------------|----------------------------------|---------|-----------------|
| blank 1 <sup>a</sup> | 0.6          | MAO       | 1500  | 2413  |       | 131                 | 62%             | 290                              | bimodal | _               |
| 1 <sup>b</sup>       | 0.6          | MAO       | 1500  | 2987  | 75    | 134                 | 65%             | 760                              | 6.5     | 0.5             |
| blank 2 <sup>a</sup> | 0.6          | TMA       | 500   | 1753  |       | 139                 | 61%             | 530                              | bimodal | _               |
| $2^b$                | 0.6          | TMA       | 500   | 1965  | 25    | 133                 | 28%             | 980                              | 5       | 0.5 - 2         |
| $3^b$                | 0.6          | TMA       | 400   | 280   | 20    | 140                 | 62%             | 1114                             | 15.7    | 1 - 10          |
| $4^b$                | 0.6          | TMA       | 300   | 162   | 15    | 139                 | 62%             | 831                              | 9       | 1-4             |

<sup>*a*</sup> Experimental conditions: heptane, 30 mL; reaction time = 1 h; T = 30 °C;  $P_{\text{ethylene}} = 1$  bar. <sup>*b*</sup> Experimental conditions: heptane, 30 mL; reaction time = 1 h; T = 30 °C;  $P_{\text{ethylene}} = 1$  bar; reaction time before polymerization = 24 h at 65 °C under stirring; PI- $\Phi_2$ OH:  $M_n = 2515$  g mol<sup>-1</sup>; [PI- $\Phi_2$ OH] = 1 mg ml<sup>-1</sup>. <sup>*c*</sup> Determined by DSC. <sup>*d*</sup> Determined by SEC (1,2,4-trichlorobenzene at 150 °C).

reduction of the Al/Fe ratio also leads to a diminution of the molar masses (run 3 and run 4).

Additionally, the morphology of the PE beads was investigated by scanning electron microscopy.

In the absence of  $PI-\Phi_2OH$  support, the so-formed PE does not exhibit any specific morphology. In contrast, both MAO and



(a): blank 1



(b): Run 1



(c): Run 3

Fig. 6 SEM pictures of PE prepared with MeDIP(2,6*i*PrPh)<sub>2</sub>FeCl<sub>2</sub> under homogeneous conditions (a) and prepared in the presence of PI- $\Phi_2$ OH (b) and (c).



Fig. 7 Pressure decrease during ethylene polymerization with MeDI-P(2,6*i*PrPh)<sub>2</sub>FeCl<sub>2</sub>/MAO under homogeneous conditions (Blank 1) and with PI- $\Phi_2$ OH (Run 1).

TMA activated catalytic systems supported with  $PI-\Phi_2OH$  formed spherical PE particles (Fig. 6).

MAO-based catalytic system enables the formation of rather well-defined PE spherical particles with a sizes of 0.5  $\mu$ m range. In the case of TMA, the size of the PE particles remains in the micron range but varies upon the experimental conditions (Al/Fe ratio) as shown in Table 2. A better control of the particle size is observed with respect to the higher Al/Fe ratio which corresponds to the higher catalytic activity. The higher the catalytic activity, the smaller the PE beads.

Concerning the polymerization kinetic, the decrease of ethylene pressure was followed by connecting the schlenk to a guard bottle charged with 1 bar of monomer. The pressure drop in homogeneous conditions (blank 1) and in the presence of PI- $\Phi_2$ OH (run 1) are represented Fig. 7.

As can be observed, the decrease of ethylene pressure in both conditions follows the same profile, showing that  $PI-\Phi_2OH$  does not modify the kinetic of ethylene polymerization. Further analyses dealing with kinetic studies in various experimental conditions are currently in progress.

#### Polymerization of ethylene using (α-diimine)nickel(II)

In order to extend this concept of supports to a large range of catalytic systems for olefin polymerization, micellar-like
Table 3 Polymerization of ethylene in the presence of the catalytic system composed of  $PI-\Phi_2OH + MAO$  or TMA and ( $\alpha$ -diimine)nickel(II)

| Run                  | n(cata)/µmol | Activator | Al/Ni | <i>T</i> /°C | Activity<br>kg/mol(C) <sup>-1</sup> h <sup>-1</sup> bar <sup>-1</sup> | Al/OH | $T_m/^{\circ}C^c$ | Xc <sup>c</sup> | $M_w^{d}$ /kg mol <sup>-1</sup> | $D^d$     | Bead<br>size/µm |
|----------------------|--------------|-----------|-------|--------------|---|-------|-------------------|-----------------|---------------------------------|-----------|-----------------|
| Blank 1 <sup>a</sup> | 5            | ТМА       | 200   | 0            | 208   |       | 131               | 52%             | 413                             | 7         |                 |
| $1^b$                | 5            | TMA       | 200   | 0            | 11  | 84    | 133               | 34%             | 406                             | $3.5^{e}$ | 1-4             |
| Blank $2^a$          | 5            | MAO       | 200   | 30           | 344   | _     | 69                | 1%              | 156                             | 2.6       |                 |
| $2^{b}$              | 5            | MAO       | 200   | 30           | 317   | 84    | 63                | 1%              | 242                             | 1.5       | 5-80            |
| Blank 3 <sup>a</sup> | 5            | MAO       | 200   | 0            | 525   |       | 126               | 38%             | 433                             | 4.8       | _               |
| 3 <sup>b</sup>       | 5            | MAO       | 200   | 0            | 61  | 84    | 122               | 31%             | 192                             | 1.4       | 0.5             |
| Blank 4 <sup>a</sup> | 5            | MAO       | 200   | -10          | 324   |       | 128               | 44%             | 490                             | 3.5       |                 |
| $4^b$                | 5            | MAO       | 200   | -10          | 90  | 84    | 126               | 40%             | 2 440                           | 1.8       | 0.5             |
| Blank 5 <sup>a</sup> | 1            | MAO       | 460   | -10          | 1341  |       | 138               | 61%             | 773                             | 5.8       |                 |
| $5^b$                | 1            | MAO       | 460   | -10          | 402   | 39    | 135               | 60%             | 1 720                           | 1.4       | 0.5             |

<sup>*a*</sup> Experimental conditions: heptane, 30 mL; reaction time = 1 h;  $T = 30 \degree C$ ;  $P_{ethylene} = 1$  bar. <sup>*b*</sup> Experimental conditions: heptane, 30 mL; reaction time = 1 h;  $T = 30 \degree C$ ;  $P_{ethylene} = 1$  bar; reaction time before polymerization = 24 h at 65 °C under stirring; PI- $\Phi$ 2OH:  $M_n = 2515$  g mol<sup>-1</sup>; [PI- $\Phi$ 2OH] = 1 mg ml<sup>-1</sup>. <sup>*c*</sup> Determined by DSC. <sup>*d*</sup> Determined by SEC (1,2,4-trichlorobenzene at 135 °C). <sup>*e*</sup> Bimodal distribution.

structures obtained from PI- $\Phi_2$ OH self-assembly have been tested as supports of nickel-based catalyst. ( $\alpha$ -diimine)nickel(II) is known to produce branched PE (chain-walking mechanism) for which the number of branches can be tuned by catalyst structure, ethylene pressure and temperature.<sup>21–23</sup> Less bulky catalysts are more resistant to chain-walking process and produce less branched PE. Therefore, nickel catalyst with relatively small ethyl substituents in *ortho* positions of aryl rings was chosen. The influence of the support and the temperature on the efficiency of ( $\alpha$ -diimine)nickel(II) have been studied; data are collected in Table 3.

Catalytic activities of  $(\alpha$ -diimine)nickel(II) in the presence of PI- $\Phi_2$ OH support vary from 11 to 402 kg PE/(mol Ni h bar) with respect to the activator and the temperature. Polymerizations activated by TMA showed generally lower activity compared to MAO activated ones.

Unlike polymerizations performed at 30 °C, for which the catalytic activities are comparable whatever the conditions, at low temperature (-10/0 °C), the catalytic activity was found to be much lower in the presence of PI- $\Phi_2$ OH support.



Fig. 8 GPC chromatograms (refractive index) of PE produced with  $(\alpha$ -diimine)nickel(II) and PI- $\Phi_2$ OH as support.

This behavior can be explained by the difficulty encountered by the catalyst to penetrate the micellar structure, thus impeding the effective formation of the active species.



(a): Blank 3



(b): Run 2



(c): Run 3

Fig. 9 SEM pictures of PE prepared with ( $\alpha$ -diimine)nickel( $\pi$ ) under homogeneous conditions (a) and prepared in the presence of PI- $\Phi_2$ OH (b) and (c).

As expected, the catalytic activity increased with the Al/Ni ratio, whatever the experimental conditions (activity = 402 kg PE/(mol Ni h bar) for MAO/Ni = 460, run 5, and activity = 90 kg PE/(mol Ni h bar) for MAO/Ni = 200, run 4). With MAO as an activator (runs 2–5), PEs with monomodal molar mass distributions and narrow dispersities, *D*, were obtained while PE with a bimodal distribution is obtained with TMA (run 1) (Fig. 8). As it could be expected, a decrease in the reaction temperature yields PEs with a higher crystallinity ratio (higher melting temperature) in agreement with a lower chain-walking rate and the formation of high molecular weight linear polyethylene (run 4).

In all cases, scanning electron microscopy revealed the formation of spherical PE beads (Fig. 9). Interestingly, the size and size distribution of the PE particles depend on the experimental conditions.

While PE particles with a broad size distribution of between 5  $\mu$ m and 80  $\mu$ m are obtained at 30 °C (run 2), small and narrow distributed PE particles (0.5  $\mu$ m) are formed at low temperature (-10 °C, run 4). These results clearly show that the PE particle size is strongly affected by the polyethylene microstructure (linear or branched).

The formation of highly linear polyethylene (high crystalline ratio) leads to the formation of a large number of particle nuclei yielding small PE particles with a narrow size distribution. Conversely, the formation of highly branched amorphous polyethylene favor the formation of large PE particles. This phenomenon can be reasonably supported by the aggregation of growing elementary particles explained by the amorphous state of the branched polyethylene.

#### Polymerization of ethylene using Ind<sub>2</sub>ZrCl<sub>2</sub>

This concept of supporting single-site catalysts was finally extended to classical metallocene. It is worth mentioning that previous attempts to trap metallocene/MAO catalytic system within PS-based micellar structures in toluene<sup>16,17</sup> lead to systems that revealed unsuccessful to produce PE beads with a controlled morphology, probably, because only few MAO was trapped by the support. In this study, Ind<sub>2</sub>ZrCl<sub>2</sub> was tested with MAO as an activator.

The two PI- $\Phi_2$ OH supports ( $M_n = 2515 \text{ g mol}^{-1}$  and  $M_n = 5843 \text{ g mol}^{-1}$ ) were used for the polymerization of ethylene using the conditions mentionned in Table 4.

Surprisingly, the catalytic activities obtained in the presence of PI- $\Phi_2$ OH supports are comparable to the one obtained in homogeneous conditions. An activity increase is even noticed in the presence of the highest molar mass PI. The molar mass and



(a): Blank 0



(b): Run 2

Fig. 10 SEM pictures of PE prepared with  $Ind_2ZrCl_2$  under homogeneous conditions (a) and prepared in the presence of  $PI-\Phi_2OH$  (b).

molar mass distribution, D, of the so-formed PE remain the same, irrespective of the experimental conditions.

As it can be seen in Fig. 10, PE beads could be readily obtained in the presence of PI- $\Phi_2$ OH supports. The size of the PE beads stays around 1  $\mu$ m irrespective of the support molar mass. This last result proves the validity of the concept that consist in using micellar structures as organic supports for metallocene catalysts.

#### Role of PI- $\Phi_2$ OH support in the production of PE beads

In order to check the presence of polyisoprene support in the soformed PE beads, differential scanning calorimetry (DSC) was first carried out. This technique did not reveal the presence of a PI phase. Dynamic mechanical analysis (DMA) was therefore performed on PE samples prepared in both homogeneous and heterogenous conditions (Fig. 11).

Such an analysis was done on PEs produced with Ind<sub>2</sub>ZrCl<sub>2</sub>. The tan  $\delta$  *versus* temperature plot shows a first peak at -114 °C, usually denoted  $\gamma$ , which corresponds to the  $T_g$  of the PE. A second peak at -55 °C is present only for the PE sample

Table 4 Polymerization of ethylene in the presence of the catalytic system composed of  $PI-\Phi_2OH + MAO$  and  $Ind_2ZrCl_2$ 

| Run         | n(cata)/µmol | Al/Zr | $M_n$ (PI- $\Phi_2$ OH)/g mol <sup>-1</sup> | Activity/kg mol(C) <sup>-1</sup> h <sup>-1</sup> bar <sup>-1</sup> | Al/OH | $\mathrm{T_m}/^{\circ}\mathrm{C}^b$ | χc <sup>c</sup> | $M_w$ <sup>d</sup> /kg mol <sup>-1</sup> | $D^d$ | Bead size/µm |
|-------------|--------------|-------|---|--|-------|-------------------------------------|-----------------|--|-------|--------------|
| Blank $0^a$ | 3            | 500   |   | 337  |       | 135                                 | 64%             | <i>n.d.</i>                              | n.d.  |              |
| $1^b$       | 3            | 500   | 2515  | 261  |       | 135                                 | 66%             | 306                                      | 4     | 1            |
| $2^b$       | 3            | 500   | 5843  | 517  |       | 136                                 | 68%             | 306                                      | 3.3   | 1            |

<sup>*a*</sup> Experimental conditions: hetpane, 60 mL; reaction time = 1 h;  $P_{\text{ethylene}} = 1$  bar. <sup>*b*</sup> Experimental conditions: hetpane, 60 mL; reaction time = 1 h;  $P_{\text{ethylene}} = 1$  bar; Reaction time before polymerization = 24 h at 65 °C under stirring [PI- $\Phi$ 2OH] = 1mg ml<sup>-1</sup>. <sup>*c*</sup> Determined by DSC. <sup>*d*</sup> Determined by SEC (1,2,4-trichlorobenzene at 150 °C).



Fig. 11 DMA analysis of PE produced with  $Ind_2ZrCl_2$  on which the  $T_g$  of polyisoprene is visible.

produced in presence of PI- $\Phi_2$ OH. This transition corresponds to the polyisoprene  $T_g$  proving that some PI is trapped within PE beads and thus that PI- $\Phi_2$ OH supports play a role in the formation of PE beads. The last transition, at 60 °C, denoted  $\alpha$ , is related with vibrational motion and reorientation within the PE crystal.<sup>24</sup>

Such an analysis was also performed on PE samples produced with MeDIP $(2,6iPrPh)_2$ FeCl<sub>2</sub> but the presence of PI phase was not revealed in the PE beads because of the high catalytic activity (Table 2, runs 1 and 2).

#### **Experimental section**

#### Materials

Isoprene, *sec*-butyllithium, benzophenone, MAO, TMA were purchased from Aldrich. Cyclohexane and heptane were dried over polystyryl-lithium and distilled under vacuum. Isoprene was dried over di-n-butylmagnesium and distilled under vacuum and kept at 5 °C. Sec-butyllithium was filtered prior to use. Benzophenone was sublimated and kept under vacuum at room temperature. TMA (2 M solution in heptane), MAO (10% w in toluene) were used as received. MeDIP(2,6-*i*PrPh)<sub>2</sub>FeCl<sub>2</sub> was synthesized as reported in the literature<sup>25</sup> and kept in a glovebox under argon atmosphere. Ind<sub>2</sub>ZrCl<sub>2</sub> was purchased from Strem and kept in a glovebox under argon atmosphere. ( $\alpha$ -diimine)nickel(II) was synthesized as reported in the literature<sup>26</sup> and kept in a glovebox under argon atmosphere.

## Synthesis of polyisoprene diphenyl alcohol terminated (PI- $\Phi_2OH$ )

A dry round bottom flask equipped with a magnetic stirrer was charged with 40 mL of cyclohexane, s-butyllithium (1.67 mL; 0.002 mol) and isoprene (5.88 mL). The flask was immersed in an oil bath at 50 °C for 2h. A solution (1M) of benzophenone in cyclohexane was then added (4 mL; 0.004 mol) and the mixture was stirred at 50 °C overnight. The polymer was precipitated into an excess of methanol, then an excess of ethanol at 30 °C to remove unreacted benzophenone and finally dried under vacuum at room temperature.  $M_n = 2515 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.07$ , <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 1.64 (CH3 of PI, b), 2.05 (CH2 of PI, m), 3.06 (H of OH, s), 5.1 (H of PI, b), 7.5–7.2 (aromatic, 10H, m).

#### Polymerization of ethylene

The desired quantity of PI- $\Phi_2$ OH support was introduced in a Schlenk tube and lyophilized during a night with dioxane. Dry heptane and activator (TMA or MAO) was added. The reactor mixture was heated to 65 °C for 24h. The reaction mixture was then connected to a 1 bar ethylene gas outlet using a rubber tube. Schlenk tube was purged by ethylene for 20 min to remove argon. Polymerization was initiated by injection of the required amount of catalyst in toluene *via* a syringe. After 1 h of polymerization, the vessel was disconnected from the ethylene outlet, and the polymer was precipitated by addition of ethanol containing 10% HCl. The precipitated polymer was filtered, washed, and dried to constant weight.

#### Analysis

<sup>1</sup>H NMR spectra were recorded using Bruker AC-400 NMR spectrometer using CDCl<sub>3</sub> at room temperature. Size exclusion chromatography (SEC) was performed in THF at 40 °C at a flow rate of 1 mL min<sup>-1</sup> using a differential refractometer (Varian) and a UV-visible spectrophotometer (Varian) operating at 254 nm and 4 TSK columns (G5000HXL (9 µm), G4000HXL (6 µm), G3000HXL (6 µm), and G2000HXL (5 µm)). Calibration was performed using linear (1,4)-polyisoprene standards.

The PE weight average molar mass  $(M_w)$  and molar mass distribution of ( $\alpha$ -diimine)nickel(II) produced PEs were determined using a Waters GPCV2000 SEC instrument, equipped with two PLgel (300 × 7.5 mm) columns, and an online viscometer and refractive index detector, at 135 °C in 1,2,4-trichlorobenzene as solvent at a flow rate of 0.9 mL min<sup>-1</sup>.

The PE weight average molar mass  $(M_w)$  and molar mass distribution of MeDIP(2,6-*i*PrPh)2FeCl<sub>2</sub> and Ind<sub>2</sub>ZrCl<sub>2</sub> produced PEs were determined using a Waters GPCV2000 SEC instrument, equipped with three columns PLgel Olexis Guard (300 × 7.5 mm), and an online viscometer and refractive index detector, at 150 °C in 1,2,4-trichlorobenzene as a solvent at a flow rate of 1 mL min<sup>-1</sup>.

PE beads were observed under scanning electronic microscopy (SEM) analyses on a JEOL JSM 2500 apparatus.

Dynamic light scattering (DLS) measurements were performed using an ALV Laser goniometer, which consists of a 22 mW HeNe linear polarized laser with 632.8 nm wavelength and an ALV-5000/EPP multiple tau digital correlator with 125 ns initial sampling time. The samples were kept at constant temperature (30 °C) during all the experiments. The accessible scattering angle range is from 10° up to 150°. However, due to difficulties in removing dust, most of the dynamic measurements were done at diffusion angles higher than 40°. The dispersions were introduced into 10 mm diameter glass cells. Dynamic light scattering measurements were evaluated by fitting the measured normalized time autocorrelation function of the scattered light intensity with the help of the constrained regularization algorithm (CONTIN), which provides the distribution of relaxation times  $\tau$ ,  $A(\tau)$ , as the inverse Laplace transform of  $g^{(1)}(t)$  function:

$$g^{(1)}(t) = \int_{0}^{\infty} A(\tau) \exp\left(-\frac{t}{\tau}\right) \mathrm{d}t \tag{1}$$

The apparent diffusion coefficient *D* was obtained by plotting the relaxation frequency,  $\Gamma$  ( $\Gamma = \tau^{-1}$ ) versus q2 where q is the wavevector defined as

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \tag{2}$$

and  $\lambda$  is the wavelength of the incident laser beam (632.8 nm),  $\theta$  is the scattering angle, and *n* the refractive index of the media. The diffusion coefficient was then determined by extrapolation to zero concentration, and hydrodynamic radius (*R*<sub>H</sub>) was calculated from the Stokes–Einstein relation

$$R_{\rm H} = \frac{k_{\rm B}T}{6\pi\eta\Gamma}q^2 = \frac{k_{\rm B}T}{6\pi\eta D_{\rm real}}$$
(3)

where  $k_{\rm B}$  is the Boltzmann constant,  $\Gamma$  the relaxation frequency, T is the temperature, and  $\eta$  is the viscosity of the medium. Dispersions used for light scattering were prepared using the following method: heptane was preliminarily filtered through a 0.22 µm PTFE membrane and added to polymer chains and the activator when necessary. The dispersions were then left under stirring for 24 h at 65 °C for complete dissolution.

The DMA analysis measurements were performed with a Thermal Analysis RSA 3 instrument using a cylindrical geometry over a temperature range of -140 to  $150 \,^{\circ}$ C at a rate of  $10 \,^{\circ}$ C min<sup>-1</sup> under nitrogen flow. All samples were scanned at a frequency of 1Hz.

#### Conclusions

In this paper, we report the use of polyisoprene end-capped with a diphenyl alcohol,  $PI-\Phi_2OH$ , as support for ethylene polymerization in an aliphatic solvent, *i.e.*, heptane. The self-assembly of these end-functionalized PI oligomers in heptane allowed us to use the formed micellar structures as organic supports for both post-metallocene and metallocene catalytic systems. Ethylene polymerizations performed in the presence of such nanoreactors lead to the formation of PE beads with a micrometric size. Remarkably, this paper shows, for the first time, that the polyethylene microstructure (linear or branched) affects the size of the so-formed PE beads (in the case of Ni catalyst) and also that such concept of organic templates can be effectively extended to metallocene catalysts, which generally require a quite high concentration of aluminic activator.

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## Polymer Chemistry

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### **P6**



# Control of morphology in olefin polymerization catalyzed by nickel diimine complexes encapsulated into polybutadiene based support

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A commercially available hydroxyl terminated low molecular *cis*-1,4-polybutadiene was modified by carboxylic functions and used as an effective support in single-site  $\alpha$ -olefin polymerization. Dynamic light scattering analysis of support solution in heptane confirmed increased ability to self-assembly of modified polybutadienes in the presence of methylaluminoxane cocatalyst (MAO).  $\alpha$ -Diimine nickel and bis(indenyl)zirconium dichloride catalysts activated by trimethylaluminium or MAO cocatalysts were encapsulated into polymer micellar aggregates and used for ethylene and octadec-1-ene polymerization. Furthermore, the effects of cocatalyst type and concentration on the micelle-formation process, activity and morphology of polyethylene (polyoctadec-1-ene) particles were investigated. In the presence of polybutadiene supports, formation of spherical micrometric PE beads was observed during MAO cocatalyzed ethylene polymerization, whereas the activity of polymerization was not decreased.

#### Introduction

Control of polymer morphology during homogeneous and heterogeneous catalysis is an important technological parameter in polyolefin industrial production. Production of spherical and uniform particles prevents from reactor fouling and also facilitates the separation of polymer from the reactor. For production of such uniform particles it is necessary to immobilize the catalyst onto inorganic or organic supports.<sup>1,2</sup> The most used inorganic supports are silica, alumina or magnesium chloride. The drawback of these supports is their insolubility in the polymer matrix, when the residual inorganic support remains in the final polymer and affects its properties.<sup>3</sup> Therefore, research is conducted to develop organic supports such as polysiloxanes,<sup>4,5</sup> polyolefins<sup>6</sup> and polystyrene.<sup>7</sup>

Another approach is utilization of end-functionalized polymers or block copolymers that can self-assemble to form micelles that can encapsulate the catalytic system and serve as a nanoreactor.<sup>8</sup> Bouilhac *et al.*<sup>9</sup> prepared benzophenone functionalized polystyrene, which proved to self-assemble in toluene. With the Fe-based catalytic system, the millimetric polyethylene beads were produced during ethylene polymerization. New supports based on polyisoprene-*block*-polymethylmethacrylate (PI-*b*- PMMA) and polyisoprene-*block*-polyethyleneoxide copolymers were synthesized by Heurtefeu *et al.*<sup>10</sup>

It was observed that the morphology of polymer particles varied with polymerization degree, concentration and type of the block copolymer. Catalytic activities of ethylene polymerization using Ind<sub>2</sub>ZrCl<sub>2</sub> as a catalyst were negatively affected at higher support concentration. In the case of bis(iminopyridyl)FeCl<sub>2</sub> catalyst any decrease of activity was observed. Recently, Heurtefeu et al. synthesized polyisoprene end-capped with a diphenyl-tertiary alcohol moiety,11 which was used for ethylene polymerization catalyzed by zirconocene, iron and nickel postmetallocenes producing micrometric beads. The best morphology was achieved using nickel diimine catalysts, which are not only highly active catalysts but also enable to control the branching of polyethylene chain due to the so-called chain-walking mechanism.12,13 Another important feature of Ni catalysts, generally observed for all late transition metal catalysts, is their lower sensitivity to polar groups presented as end functions in supports.

In this work, we want to expand the "micelle based" concept on commercially available functionalized polymers to overcome the usually tedious synthetic procedure used for the preparation of previously described supports. Hydroxyl terminated lowmolecular *cis*-1,4-polybutadiene (Sartomer) was selected for its solubility in aliphatic solvents and chemically modified. Nickel diimine complexes (Fig. 1) or bis(indenyl)zirconium dichloride were activated either by MAO or TMA encapsulated into polymer micelles. New supports were also compared with previously used PI-*b*-PMMA copolymers. The effect of type and concentration of the support on catalyst activity and the final morphology of PE particles were investigated.

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Fig. 1 Structure of nickel-diimine catalysts.

#### **Results and discussion**

#### Support synthesis

To overcome the tedious preparation procedure of supports we tried to utilize commercially available hydroxyl-terminated polybutadiene (PBD–OH). However, PBD–OH itself is not able to stabilize MAO dispersed in heptane and immediate precipitation of MAO was observed from PBD–OH solutions demonstrating that PBD–OH does not form micelles in this solvent. Therefore, we decided to transform aliphatic hydroxyl end-groups of PBD–OH to carboxylic groups which were found to promote self-assembly when connected as end-groups of polystyrene chains.<sup>9</sup> Firstly, polybutadiene ended by aliphatic carboxylic groups (PBD–MA) was prepared by a reaction of PBD–OH and maleic anhydride in toluene at 100 °C (Scheme 1).

Three molar excess of maleic anhydride was used to shift the equilibrium of reaction in favor of products and to decrease coupling of chains. <sup>1</sup>H NMR analysis confirmed high (>80%) conversion of polybutadiene hydroxyl end-functions ( $\delta = 3.65$  ppm) to carboxylic acid functions (Fig. 2). SEC-MALLS results showed the appearance of two peaks, the major one corresponding to the desired PBD–MA product and the minor one with doubled molar mass corresponding to a dimer formed by coupling reaction between the unreacted carboxylic group of PBD–MA and another PBD–OH chain (Table 1).

Secondly, preparation of polybutadiene with two aromatic carboxylic end groups (PBD–TRIMA) was attempted by reaction of PBD–OH with 20 eq. of trimesoyl chloride at -60 °C in THF in the presence of triethylamine followed by hydrolysis in water (Scheme 2).

<sup>1</sup>H NMR analysis shows quantitative transformation of hydroxyl end-groups to aromatic dicarboxylic ones (Fig. 3). SEC-MALLS analysis showed a small amount (2.5%) of dimer along with the main product (Table 1).

#### DLS study of self-assembly of the PBD-MA support in heptane

Self-assembly of functionalized polybutadiene was investigated in heptane solution by dynamic light-scattering (DLS). The  $R_{\rm H}$ 







Fig. 2 <sup>1</sup>H NMR spectra of PBD–MA support.

values were calculated from the decay times using the Stokes-Einstein equation (eqn (4)). These relaxation times were determined by applying the CONTIN analysis<sup>14</sup> to the autocorrelation functions. PBD-MA solutions were prepared using the P2 protocol. In the first series of experiments, the support solutions of different concentrations (0.5, 1 and 2 mg mL<sup>-1</sup>) in heptane were prepared. Solutions did not show any sedimentation, however, laser diffusion intensity was too low to confirm any micelle structure formation. The only reliable results were obtained for 2 mg mL<sup>-1</sup> support concentration at angles of 30-60° where the presence of free molecules and formation of particles with  $R_{\rm H} = 107$  nm were observed (Fig. 4). However, the non-zero signal of the autocorrelation function at higher relaxation times as well as non-possibility to fit decay rate versus square scattering vector plot indicate that PBD-MA is not capable of forming well defined structures and shows the presence of different populations of aggregates with non-spherical shapes. The effect of MAO addition on formation of micelles was then investigated. The three solutions of different concentration were prepared and analyzed by DLS. The DLS analysis ( $c_{PBD-}$  $_{MA} = 1 \text{ mg mL}^{-1}$ ) confirmed the formation of a single population of particles with  $R_{\rm H}$  of 70 nm without any sedimentation (Fig. 5). The high polarity of MAO has therefore a positive effect on nano-object formation.

This effect can be explained by the stabilization of particles by increased polarity of the system and also by chemical interactions between the carboxylic group of the support and aluminium atoms of MAO, the latter acting as a nucleating agent.

## DLS study of self-assembly of the PBD-TRIMA support in heptane

To improve the ability of the PBD–MA to form micellar structures in heptane (without MAO) another PBD support with more polar end function was synthesized by reaction of PBD–OH with trimesoyl chloride (PBD–TRIMA). The laser diffusion intensity of PBD–TRIMA solution in heptane (prepared using the **P2** protocol) was higher than in the case of the PBD–MA support and a linear variation of relaxation frequency  $\Gamma$  with square scattering vector  $q^2$  passes through the origin, which is the hallmark of a translational diffusive process typical for spherical objects (Fig. 6).

| Table 1 | Molar mass, | dispersity an | d extent of | f coupling | reaction of P | BD-MA | and PBD- | -TRIMA | supports |
|---------|-------------|---------------|-------------|------------|---------------|-------|----------|--------|----------|
|---------|-------------|---------------|-------------|------------|---------------|-------|----------|--------|----------|

| Support   | Method                                  | $M_{ m n}/ m g\ mol^{-1}$ | $M_{ m w}/M_{ m n}$ | Coupling |
|-----------|---|---------------------------|---------------------|----------|
| PBD-MA    | Theor.                                  | 4730                      | 1.05                |          |
|           | <sup>1</sup> H NMR (CDCl <sub>3</sub> ) | 5180                      |                     |          |
|           | SEC-MALLS (THF)                         | 4190                      | 1.10                | 9.8%     |
| PBD-TRIMA | Theor.                                  | 4820                      | 1.05                |          |
|           | <sup>1</sup> H NMR (CDCl <sub>3</sub> ) | 5520                      |                     |          |
|           | SEC-MALLS (THF)                         | 4770                      | 1.06                | 2.5%     |



Scheme 2 Synthesis of PBD–TRIMA support.



Fig. 3 <sup>1</sup>H NMR spectra of PBD–TRIMA support.



Fig. 4 Auto-correlation function (circles) and relaxation times distribution (solid line) of PBD–MA ( $c = 2 \text{ mg mL}^{-1}$ ) at  $\theta = 60^{\circ}$  in heptane. Dependency of the relaxation frequency  $\Gamma$  on the square scattering vector  $q^2$  inserted.



**Fig. 5** Auto-correlation function (circles) and relaxation times distribution (solid line) of PBD–MA ( $c = 1 \text{ mg mL}^{-1}$ ) at  $\theta = 90^{\circ}$  in heptane with MAO and dependency of the relaxation frequency  $\Gamma$  on the square scattering vector  $q^2$ (inserted).



Fig. 6 Auto-correlation function (circles) and relaxation times distribution (solid line) of PBD–TRIMA ( $c = 2 \text{ mg mL}^{-1}$ ) at  $\theta = 90^{\circ}$  in heptane and dependency of the relaxation frequency  $\Gamma$  on square scattering vector  $q^2$  (inserted).

When MAO was added to PBD–TRIMA solution, the  $R_{\rm H}$  of particles increased to 40.3 nm (Fig. 7) showing a probable stabilization of MAO by the PBD–TRIMA without any sedimentation. Tailing of the DLS peak at higher relaxation times also shows the formation of a small proportion of larger aggregates.

## DLS study of self-assembly of PBD-MA and PBD-TRIMA support solution with TMA in heptane

The ability to form micelles of PBD–MA and PBD–TRIMA in heptane in the presence of trimethylaluminium (TMA) was also investigated.

The collected DLS data showed predominantly the formation of large aggregates corresponding to the peaks at 1460 nm (PBD–MA) and 888 nm (PBD–TRIMA, Fig. 8), respectively. A



Fig. 7 Auto-correlation function (circles) and relaxation times distribution (solid line) of PBD–TRIMA ( $c = 1 \text{ mg mL}^{-1}$ ) at  $\theta = 90^{\circ}$  in heptane with MAO and dependency of the decay rate  $\Gamma$  on square scattering vector  $q^2$  (inserted).



Fig. 8 Auto-correlation function (circles) and relaxation times distribution (solid line) of PBD–TRIMA ( $c = 1 \text{ mg mL}^{-1}$ ) at  $\theta = 80^{\circ}$  in heptane with TMA. Inset: dependency of the relaxation frequency  $\Gamma$  on square scattering vector  $q^2$ .

second population of peaks at 186 nm (PBD–MA) and 91 nm (PBD–TRIMA) was also observed. These minor populations could correspond to nano-objects formed by a core of TMA surrounded by PBD–MA and PBD–TRIMA respectively. The dependency of relaxation frequency  $\Gamma$  on  $q^2$  could not be fitted with a linear curve in the case of the PBD–MA support indicating that formed objects are not spherical.

In the case of the PBD–TRIMA (Fig. 8),  $\Gamma$  vs. squared scattering vector plot of population corresponding to a peak at 91.4 nm could be linearly fitted suggesting the formation of spherical particles with  $R_{\rm H}$  of about 85 nm.

## Polymerization of ethylene with (An, Me<sub>3</sub>)NiBr<sub>2</sub>/MAO in the presence of functionalized polybutadiene supports

Polymerizations of ethylene were carried out in heptane using the (An, Me<sub>3</sub>)NiBr<sub>2</sub> catalyst (Fig. 1) with small aryl substituents which suppress the extent of chain-walking and lead to semicrystalline polyethylenes with low branch content<sup>15</sup> (Table 2). For the same reason reaction temperature was set to 0 °C. MAO was used as a cocatalyst and procedure **P2** (see Experimental section) as a protocol for micelles formation was employed. Depending on the viscosity of reaction mixture, the polymerization was quenched after 0.5 h (in the case of insufficient agitation) or after one hour. It is worth noting that the presence of both PBD–MA and PBD–TRIMA supports did not decrease the activity of ethylene polymerization certainly due to the lower oxophilicity of nickel catalyst. Comparison of supported and homogeneous polymerization shows a difference in morphology of the polyethylene particles (Fig. 9).

In the presence of a polybutadiene support, the separated and regularly sized particles were formed. In the case of a non-supported polymerization (exp. 1 and 2), the particles are connected with fibres and often form clusters, which cause difficulties in the polymerization process, such as increase of viscosity and ineffective agitation. Crystallinity of polyethylene varied from 31 to 54% (1. run data collection). In the case of polymerizations in the presence of support, higher PE crystallinity was always observed compared to homogeneous polymerizations, suggesting that micelles presumably facilitate the crystallization of spatially restricted PE chains or the support behaves as a nucleation agent. The presence of the support also influenced slightly the microstructure of formed PE affording more linear chains that can easily form the crystalline phase as further confirmed by higher melting temperatures and higher heat of fusion (Table 1, exp. 3, 4, 5 and 8 vs. exp. 1). Molar mass decreased with an increase in support concentration from 265 kg mol<sup>-1</sup> for  $c_{\text{supp.}} = 0.5$  mg mL<sup>-1</sup> to  $103 \text{ kg mol}^{-1}$  for  $c_{\text{supp}} = 2 \text{ mg mL}^{-1}$  in the case of the PBD-MA support (exp. 3-5). If all active sites are encapsulated by the support and polymerization can proceed inside the micelles only, the higher support concentration provides a higher number of active species which produce shorter polymer chains. However, in the case of the PBD-TRIMA support (exp. 6-8) this effect was not observed and the molar mass of polyethylene seems to be independent of the support concentration.

## Polymerization of ethylene with (An, Me<sub>3</sub>)NiBr<sub>2</sub>/MAO in the presence of PI-*b*-PMMA copolymers

For comparative reasons, ethylene polymerization with a previously studied support system based on PI-*b*-PMMA copolymers was performed<sup>10</sup> (Table 3). The activity of ethylene polymerization catalyzed by (An, Me<sub>3</sub>)NiBr<sub>2</sub>/MAO was not affected by the presence of PI-*b*-PMMA block copolymers showing low sensitivity of nickel catalyst to polar compounds, similarly as observed earlier for the bis(iminopyridyl) iron catalyst and in contrast with Ind<sub>2</sub>ZrCl<sub>2</sub> which was dramatically deactivated at higher PI-*b*-PMMA concentrations.<sup>10</sup> SEM analysis of PE samples prepared by polymerization with PI-*b*-PMMA supports showed the formation of micrometric beads similar in size to those formed when the polybutadiene supports were used (Fig. 10).

However, formation of fibers interconnecting the particles suggests lower morphology control. Crystallinity of polyethylenes increased with support concentration similarly to polybutadiene supported polymerizations.

Molar mass varied from 75 to 88 kg mol<sup>-1</sup> and was not influenced by the support concentration in the range 0.5-1 mg mL<sup>-1</sup>. Significantly higher molar mass polyethylene was obtained at the lowest PI-*b*-PMMA concentration (exp. 9) suggesting again the inverse proportion between the number of micelles and length of polymer chains.

Table 2 Polymerization of ethylene catalyzed by (An, Me<sub>3</sub>)NiBr<sub>2</sub>/MAO at homogeneous conditions and with PBD-MA and PBD-TRIMA supports<sup>a</sup>

| Exp. | Support   | $c_{\text{supp}}/\text{mg mL}^{-1}$ | t <sub>p</sub> /h | $A/kg^{-1} mol^{-1} h^{-1} bar^{-1}$ | $X_{c}^{b}$ (%) | $T_{\rm m}{}^b/^{\circ}{\rm C}$ | $N^{c}$ | $M_{\rm n}{}^d/{\rm kg}~{\rm mol}^{-1}$ | $M_{\rm w}/M_{\rm n}^{\ d}$ | Morphology |
|------|-----------|-------------------------------------|-------------------|--------------------------------------|-----------------|---------------------------------|---------|---|-----------------------------|------------|
| 1    |           | 0                                   | 0.5               | 680                                  | 31              | 126                             | 18      | 187.8                                   | 39                          | PARTIAL    |
| 2    |           | 0                                   | 0.5               | 865                                  | 37              | 126                             |         | 69.8                                    | 4.0                         | PARTIAL    |
| 3    | PBD-MA    | 0.5                                 | 1                 | 961                                  | 46              | 132                             | 8       | 264.8                                   | 3.1                         | GOOD       |
| 4    |           | 1                                   | 1                 | 811                                  | 42              | 130                             | 12      | 173.9                                   | 3.5                         | GOOD       |
| 5    |           | 2                                   | 1                 | 973                                  | 49              | 132                             | 9       | 103.3                                   | 3.1                         | GOOD       |
| 6    | PBD-TRIMA | 0.5                                 | 1                 | 745                                  | 49              | 130                             |         | 119.6                                   | 3.4                         | GOOD       |
| 7    |           | 1                                   | 1                 | 793                                  | 48              | 131                             |         | 123.6                                   | 4.2                         | GOOD       |
| 8    |           | 2                                   | 1                 | 665                                  | 54              | 135                             | 5       | 136.1                                   | 3.7                         | GOOD       |

<sup>*a*</sup>  $n_{CAT} = 5 \mu mol; T = 0 °C, p_{ethylene} = 1 bar; solvent: heptane; cocat.: MAO; Al/Ni =200; V_{TOT} = 20 mL, protocol of micelles formation:$ **P2**.<sup>*b*</sup> Crystallinity and melting temperature determined by DSC. <sup>*c*</sup> The number of branches per 1000 C atoms determined by <sup>1</sup>H NMR spectroscopy.<sup>*d*</sup> Determined by HT-SEC. <sup>*e*</sup> Determined by SEM.



Exp. 1



Exp. 5



Fig. 9 SEM pictures of PE prepared with  $\alpha$ -diimine nickel catalyst under homogeneous conditions (1) and in the presence of PBD–MA (5) or PBD–TRIMA (7) support.

## Effect of activator type and concentration on activity of ethylene polymerization

Beside MAO, we investigated also TMA which is known to be an efficient cocatalyst of nickel complexes even at low Al/Ni ratios.<sup>16,17</sup> Bouilhac *et al.* further showed that a small amount of benzoic acid added to TMA leads to MAO-like structure formation and increase of polymerization activity.<sup>18</sup> We followed this strategy in an effort to prepare an activator which will be efficient at low Al/Ni ratios, providing comparable activity and control of morphology to MAO. Results confirmed that TMA with benzoic acid (BA) has a slightly higher activity and better control of morphology than TMA itself, but still lower than the activity obtained with MAO at an Al/Ni ratio of 200 (Table 4). Nevertheless, at low Al/Ni ratios (25–50) the activity of polymerization of the TMA/BA activator is even higher than in the case of MAO, which requires higher Al/Ni ratios.

The effect of the activator concentration on activity and polymer morphology was investigated. Three different activators were used in different ratios. As a protocol of micelles formation, procedure 1 (P1) was used. This procedure included 24–72 h of agitation, which was necessary for the reaction between TMA and benzoic acid. In the case of MAO, the activity was very sensitive to the Al/Ni ratio and a large decrease of activity was observed (Table 4, exp. 5, 16 and 18). Comparison of activities of TMA and MAO proved lower efficiency of TMA at high Al/Ni ratios (exp. 15), but at low Al/Ni ratios the activity of TMA did not decrease (exp. 20). In the case of TMA, the morphology of resulting polymers is comparable with those where no support was added, which can be explained by the poor ability of TMA to stimulate the formation of micelles, as already discussed. Significant improvement of morphology was observed in the presence of TMA combined with benzoic acid (exp. 17 and 19) and particles resembling those obtained in MAO cocatalyzed polymerizations were prepared.

## Polymerization of ethylene with $Ind_2ZrCl_2$ in the presence of PBD-MA support

To test the new polybutadiene support with other catalysts we selected Ind<sub>2</sub>ZrCl<sub>2</sub>. This catalyst was tested by Hertefeu *et al.* with PI<sub>16</sub>-*b*-PMMA<sub>4</sub> support observing several orders of magnitude decrease of activity.<sup>10</sup> Contrary to that, activity of

Table 3 Polymerization of ethylene in the presence of catalytic system (An, Me<sub>3</sub>)NiBr<sub>2</sub>/MAO and PI-b-PMMA supports<sup>a</sup>

| Exp.     | Support  | $c_{\text{supp.}}/\text{mg mL}^{-1}$ | t <sub>p</sub> /h | $A / \mathrm{kg^{-1}} \mathrm{mol^{-1}} \mathrm{h^{-1}} \mathrm{bar^{-1}}$ | $X_{c}^{b}$ (%) | $T_{\rm m}{}^b/^{\circ}{\rm C}$ | $N^{c}$ | $M_{\rm n}^{d}$ /kg mol <sup>-1</sup> | $M_{\rm w}/{M_{\rm n}}^d$ | Morphology <sup>e</sup>  |
|----------|--|--------------------------------------|-------------------|--|-----------------|---------------------------------|---------|---------------------------------------|---------------------------|--------------------------|
| 9        | PI <sub>16</sub> - <i>b</i> -PMMA <sub>4</sub>   | 0.1                                  | 0.5               | 898  | 31              | 125                             |         | 208.6                                 | 3.1                       | GOOD/PART.               |
| 10<br>11 | $PI_{16}$ - <i>b</i> -PMMA <sub>4</sub><br>$PI_{16}$ - <i>b</i> -PMMA <sub>4</sub>                 | 0.5<br>1                             | 0.5               | 743  | 32<br>44        | 124<br>131                      | 20      | 75.7<br>80.5                          | 3.3<br>4.1                | PARTIAL                  |
| 12<br>13 | PI <sub>71</sub> - <i>b</i> -PMMA <sub>10</sub><br>PI <sub>71</sub> - <i>b</i> -PMMA <sub>10</sub> | 0.5<br>1                             | 0.66<br>1         | 761<br>595   | 33<br>39        | 125<br>132                      | 20      | 75.2<br>88.7                          | 3.8<br>3.3                | GOOD/PART.<br>GOOD/PART. |

<sup>*a*</sup>  $n_{CAT} = 5 \mu mol; T = 0 \, ^{\circ}C, p_{ethylene} = 1$  bar; solvent: heptane; cocat.: MAO; Al/Ni= 200;  $V_{TOT} = 20 \, \text{mL}$ , protocol of micelles formation: P2. <sup>*b*</sup> Determined by DSC. <sup>*c*</sup> The number of branches per 1000 C atoms determined by <sup>1</sup>H NMR spectroscopy. <sup>*d*</sup> Determined by HT-SEC. <sup>*e*</sup> Determined by SEM.

TOPEE





Exp. 12

Fig. 10 SEM pictures of PE prepared with  $\alpha$ -diimine nickel catalyst in the presence of PI-*b*-PMMA supports.

ethylene polymerization catalyzed by  $Ind_2ZrCl_2$  in the presence of PBD–MA support is decreased only to 60% of the value obtained without support (Table 5). It could be explained by the much lower content of oxygen containing groups in PBD–MA compared to the PI-*b*-PMMA copolymer whose ester groups easily deactivate the zirconium catalyst.

SEM analysis showed the formation of cauliflower-like structures in the presence of PBD–MA in contrast to spherical and separated particles observed when the  $\alpha$ -diimine nickel catalyst was used (*vice supra*). However, the difference in morphology between supported (exp. 22) and blank polymerization (exp. 21) is appreciable (Fig. 11).

#### Polymerization of octadec-1-ene

Nickel diimine catalysts are known to polymerize higher  $\alpha$ -olefins in a living/controlled manner.<sup>19-21</sup> Due to chain-walking they also enable 1, $\omega$ -enchainment of  $\alpha$ -olefins leading to formation of polyethylene like segments that are capable to crystallize. The combination of both features could represent an interesting way for preparation of a polymer with controlled molar mass and morphology at the same time. Therefore, we decided to investigate the polymerization of octadec-1-ene with selected Ni catalysts differing in substituent bulkiness which influence the extent of chain-walking (Fig. 1)

A decrease of conversion with respect to bulkiness of anchored substituents at homogeneous conditions was observed. The effect of support addition on conversion is significant in the case of (An, Me<sub>3</sub>)NiBr<sub>2</sub> catalyst. In all cases semicrystalline poly-(octadec-1-ene)s were prepared (Fig. 12 and Table 6) with crystallinity between 1 and 37% depending on temperature and bulkiness of  $\alpha$ -diimine catalysts. In the case of polymerization with (An, Me<sub>3</sub>)NiBr<sub>2</sub> and (An, iPr<sub>2</sub>)NiBr<sub>2</sub> catalysts (exp. 23–26) precipitation of polymer during the polymerization was not

Table 4 Effect of the activator and Al/Ni ratio on activity of the ethylene polymerization in the presence of PBD–MA support<sup>a</sup>

| Exp.            | Cocat. | Al/Ni | $t_{\rm p}/{\rm h}$ | $c_{\rm PBD-MA}/{\rm mg}~{\rm mL}^{-1}$ | $A/kg^{-1} mol^{-1} h^{-1} bar^{-1}$ | $X_{c}^{b}$ (%) | $T_{\rm m}{}^b/^{\circ}{\rm C}$ | $N^{c}$ | $M_{\rm n}{}^d/{\rm kg}~{\rm mol}^{-1}$ | $M_{\rm w}/{M_{\rm n}}^d$ | Morphology <sup>e</sup> |
|-----------------|--------|-------|---------------------|---|--------------------------------------|-----------------|---------------------------------|---------|---|---------------------------|-------------------------|
| 5               | MAO    | 200   | 1                   | 2                                       | 973                                  | 49              | 132                             | 9       | 103.3                                   | 3.1                       | GOOD                    |
| $14^{f}$        | TMA/BA | 200   | 1                   | 2                                       | 286                                  | 46              | 132                             | 5       |   |                           | GOOD                    |
| 15              | TMA    | 200   | 1                   | 2                                       | 116                                  | 48              | 133                             | 7       |   |                           | PARTIAL                 |
| 16              | MAO    | 50    | 1                   | 1                                       | 273                                  | 57              | 136                             |         | 153.8                                   | 2.6                       | GOOD                    |
| 17 <sup>f</sup> | TMA/BA | 50    | 1                   | 1                                       | 210                                  | 51              | 134                             |         | 137.7                                   | 3.0                       | GOOD/PART.              |
| 18              | MAO    | 25    | 1                   | 0.5                                     | 124                                  | 62              | 137                             |         |   |                           | GOOD/PART.              |
| 19 <sup>f</sup> | TMA/BA | 25    | 0.5                 | 0.5                                     | 361                                  | 55              | 134                             |         | 165.7                                   | 2.6                       | GOOD/PART.              |
| 20              | TMA    | 25    | 0.5                 | 0.5                                     | 322                                  | 57              | 132                             |         | _                                       | _                         | PARTIAL                 |

 $^{a}$   $n_{CAT} = 5 \mu mol; T = 0 °C, p_{ethylene} = 1 bar; solvent: heptane; <math>V_{TOT} = 20 \text{ mL}$ , protocol of micelles formation: P1.  $^{b}$  Determined by DSC.  $^{c}$  The number of branches per 1000 C atoms determined by <sup>1</sup>H NMR spectroscopy.  $^{d}$  Determined by HT-SEC.  $^{e}$  Determined by SEM.  $^{f} n_{TMA}/n_{BA} = 5/1$ .

| Table 5                | Table 5Polymerization of ethylene with $Ind_2ZrCl_2$ with MAO <sup>a</sup> |                                      |   |                       |                                 |                         |  |  |  |  |
|------------------------|--|--------------------------------------|---|-----------------------|---------------------------------|-------------------------|--|--|--|--|
| Exp.                   | Support  | $c_{\text{supp.}}/\text{mg mL}^{-1}$ | $A/\mathrm{kg}^{-1} \mathrm{mol}^{-1} \mathrm{h}^{-1}\mathrm{bar}^{-1}$ | $X_{\rm C}^{\ b}$ (%) | $T_{\rm m}{}^b/^{\circ}{\rm C}$ | Morphology <sup>c</sup> |  |  |  |  |
| 21 <sup>10</sup><br>22 | NO<br>PBD–MA   | 0<br>2                               | 1220<br>717   | 64<br>59              | 135<br>138                      | BAD<br>Part./Bad        |  |  |  |  |

<sup>*a*</sup>  $t_p = 1$  h;  $p_{\text{ethylene}} = 1$  bar; T = 30 °C;  $n_{\text{cat}} = 1$  µmol; solvent: heptane; cocat. MAO; Al/Zr = 1000;  $V_{\text{TOT}} = 20$  mL; protocol of micelles formation: **P2**. <sup>*b*</sup> Determined by DSC. <sup>*c*</sup> Determined by SEM.



Exp. 22

Fig. 11 SEM images of PE prepared with  $Ind_2ZrCl_2$  catalyst at homogeneous conditions (21) and in the presence of the PBD–MA support (22).

observed and the morphology is driven by the termination procedure only (precipitation into EtOH).

When (An, tBu)NiBr<sub>2</sub> (the catalyst with the most bulky substituents) was used, the higher proportion of linear PE-like



Fig. 12 DSC curves of poly(octadec-1-ene)s obtained by polymerization with different  $\alpha$ -diimine nickel catalysts in the presence of PBD–MA support.

segments in polyoctadecene was formed, which led to higher content of the crystalline phase (comparable with PE) and precipitation of polymer particles during the polymerization. However, the presence of the support did not lead to improvement of polymer morphology when compared with the blank experiment (Fig. 13). The positive effect of the support on polyoctadecene's microstructure as studied by 'H NMR was not proved in contrast to supported ethylene polymerization (Table 6, exp. 27 *vs.* exp. 30 and 31) and conversely higher melting temperatures were obtained in the non-supported system (exp. 27 and 28 *vs.* exp. 29–31).

#### **Experimental section**

#### Materials

The manipulation of air-sensitive compounds was done by Schlenk techniques. Chlorobenzene, toluene, and tetrahydrofuran were dried over CaH<sub>2</sub>, polystyryl-lithium and Na/benzophenone, respectively, and distilled under vacuum. Heptane was refluxed over sodium metal for 6 hours and distilled under argon. Octadec-1-ene (Aldrich) was dried over CaH<sub>2</sub> and distilled under vacuum. Ethylene was purified with molecular sieves 4A and 13X. MAO (Aldrich, 10 wt% in toluene) and TMA (Aldrich, 2 M solution in heptane) were used as received. Bis(indenyl)zirconium dichloride was purchased from Strem. Nickel diimine complexes (An, Me<sub>3</sub>)NiBr<sub>2</sub>, (An, iPr<sub>2</sub>)NiBr<sub>2</sub>, and (An, tBu)NiBr<sub>2</sub> were synthesized as reported in the literature<sup>19,22</sup> and kept under a N<sub>2</sub> atmosphere. Chlorobenzene solutions of these catalysts were kept under nitrogen in the fridge. Hydroxyl end-functionalized cis-1,4-polybutadiene SARTOMER PRO 8605/LGH036 (PBD-OH,  $M_n = 4630 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.05$ ; -OH ratio = 98.78%) was generously provided by Sartomer CZ and used as received. Poly(isoprene-block-methylmethacrylate) copolymers  $PI_{16}$ -b-PMMA<sub>4</sub> ( $M_n = 1250 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.09$ , 16 isoprene units, 4 methylmethacrylate units) and PI71-b-PMMA10  $(M_{\rm n} = 5490 \text{ g mol}^{-1}, M_{\rm w}/M_{\rm n} = 1.06, 71 \text{ isoprene units}, 10 \text{ methyl}^{-1}$ methacrylate units) supports were prepared according to ref. 10. PBD-OH as well as its other derivatives PBD-MA, PBD-TRIMA and PI-b-PMMA supports were stored in the freezer at -20 °C. Benzoic acid (Aldrich), maleic anhydride (Janssen Chimica) and triethylamine (TEA) (Aldrich) were used as received. Trimesoylchloride (Alfa Aesar) was stored in a glove box at -20 °C and used as received.

#### Support synthesis

**Maleic anhydride terminated polybutadiene (PBD–MA).** A 250 mL Schlenk flask was charged by 10.1 g (2.1 mmol) of PBD–OH, 0.64 g (6.4 mmol, 3 eq.) of maleic anhydride and by 10 mL of dried toluene and stirred and heated to 100 °C for 4 h. The

| Exp. | Cat.                | Supp.     | $c_{\text{supp.}}/\text{mg mL}^{-1}$ | $T/^{\circ}C$ | $t_{\rm p}/{\rm h}$ | $Y_{\rm w}$ (%) | $X_{c}^{b}$ (%) | $T_{\rm m}^{\ \ b}$ | $N^c$ | Morphology |
|------|---------------------|-----------|--------------------------------------|---------------|---------------------|-----------------|-----------------|---------------------|-------|------------|
| 23   | An, Me <sub>3</sub> | NO        | 0                                    | 0             | 5.5                 | 98              | 1               | 41                  | _     | BAD        |
| 24   | An, Me <sub>3</sub> | PBD-MA    | 2                                    | 25            | 24                  | 27              | 13              | 45                  |       | PART./BAD  |
| 25   | An, $iPr_2$         | PBD-MA    | 1                                    | 25            | 5.5                 | 54              | 19              | 41                  |       | BAD        |
| 26   | An, $iPr_2$         | PBD-TRIMA | 1                                    | 20            | 5                   | 26              | 20              | 46                  |       | BAD        |
| 27   | An, tBu             | NO        | 0                                    | 0             | 17.5                | 21              | 32              | 90                  |       | PART./BAD  |
| 28   | An, tBu             | NO        | 0                                    | 20            | 5                   | 26              | 37              | 93                  | 25    | PART./BAD  |
| 29   | An, tBu             | PBD-MA    | 2                                    | 0             | 23                  | 33              | 28              | 73                  |       | PART./BAD  |
| 30   | An, tBu             | PBD-MA    | 2                                    | 20            | 5                   | 37              | 32              | 76                  | 26    | PART./BAD  |
| 31   | An, tBu             | PBD-TRIMA | 1                                    | 20            | 5                   | 60              | 32              | 77                  | 32    | PART./BAD  |

**Table 6** Polymerization of octadec-1-ene using nickel diimine complexes activated by MAO at homogeneous conditions and with PBD–MA and PBD–TRIMA supports<sup>*a*</sup>

<sup>*a*</sup>  $n_{CAT} = 5 \,\mu$ mol; [C18] = 0.2 M; cocat: MAO, Al/Ni = 200, solvent: heptane;  $V_{TOT} = 20 \,\text{mL}$ , protocol of micelles formation: **P2**. <sup>*b*</sup> Determined by DSC. <sup>*c*</sup> The number of branches per 1000 C atoms determined by <sup>1</sup>H NMR spectroscopy. <sup>*d*</sup> Determined by SEM.

product was precipitated in 400 mL of ethanol and stirred for several hours. The ethanol phase was carefully drawn off and the product was dried for 48 h in the vacuum oven at 70  $^{\circ}$ C, yield 84%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)— $\delta$  (ppm) = 0.88 (m); 1.25 (m) + 1.41 (m) (– $CH_2$ – of PBD); 2.02 (– $CH_2$ – of PBD, m); 3.67 (–OH very low intensity, s); 4.30 (– $CH_2$ –COO–, m); 4.97 (m) + 5.34 (m) + 5.56(m) (=CH– of PBD), 6.23 (m) + 6.39 (m) + 6.48 (m) (=CH– of maleic acid function) [2.35; 3.80; 3.93; 7.17—residual peaks corresponding to toluene and ethanol (intensity < 0.1)].

Trimesoic acid terminated polybutadiene (PBD–TRIMA). The 250 mL triple necked flask equipped with a dropping funnel and a valve was charged by 6.7 g (25 mmol) trimesoyl chloride (20 eq. to PBD–OH) and purified by a few vacuum-N<sub>2</sub> cycles. Then 20 mL of dry THF and 0.3 mL (2.15 mmol) of TEA was added. The flask was immersed in the bath and kept at the temperature of -60 °C. PBD–OH solution (5.8 g (1.27 mmol) of PBD–OH in 150 mL of dry THF) was slowly (5 h) added dropwise into trimesoylchloride solution and then let slowly warm to room temperature and stirred overnight (20 h). Then the bath was tempered to -10 °C and reaction was quenched by 21 mL of TEA (2 eq. to COCl groups) and 3.8 mL of H<sub>2</sub>O (2 eq. to COCl groups). The product was stirred for 22 h and then THF was evaporated. The solid part was dissolved in 200 mL of toluene and filtered through a frit. The support solution was

concentrated to 20 mL and precipitated in methanol. The PBD– TRIMA support was then separated by centrifugation and dried under vacuum at 60 °C. Finally, the purification by column chromatography was used. The chromatography column ( $5 \times 18$ cm) was charged by silica (mesh 100–200), and ethylacetate/ cyclohexane (40/60) was used as a mobile phase. The purity of acquired fractions was analyzed by <sup>1</sup>H NMR.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)— $\delta$  (ppm) = 0.87 (m); 1.25 (m) + 1.43 (m) (–CH<sub>2</sub>– of PBD); 2.02 (m) (–CH<sub>2</sub>– of PBD); 4.40 (s) (–CH<sub>2</sub>–COO–); 4.95 (s) + 5.34 (m) + 5.56(m) (=CH– of PBD), 8.97 (s) + 9.03 (s) (=CH– of trimesic acid function,), [3.72 + 4.00—residual peaks (intensity < 0.08)].

#### Protocols of micelles formation

**P1**: a support (10, 20 or 40 mg) was introduced into the Schlenk flask equipped with the magnetic stirrer and purified by vacuum- $N_2$  cycles. 20 mL of solvent (and octadec-1-ene in the case of its polymerization) was then added. After dissolution of the support the flask was immersed into the ice bath and kept at 0 °C for 15 min. 0.6 mL of MAO (or TMA) (200 eq. to catalyst) was added dropwise. The flask was then immersed into an oil bath and was stirred at 60 °C for 24–72 h. The stirring solution was slowly cooled to room temperature and then tempered to the polymerization temperature.

 (An, tBu)NiBr<sub>2</sub>, 20°C, NO supp.
 (An, tBu)NiBr<sub>2</sub>, 20°C, PBD-MA

 (An, tBu)NiBr<sub>2</sub>, 20°C, PBD-MA
 (An, tBu)NiBr<sub>2</sub>, 20°C, PBD-MA

Fig. 13 SEM pictures of polyoctadecene prepared with  $\alpha$ -diimine nickel catalysts under homogeneous conditions and in the presence of PBD–MA support.

**P2**: the desired amount of support (typically 15–60 mg) was introduced into a 15 mL Schlenk flask and purified by vacuum- $N_2$  cycles. The desired amount of MAO (or TMA) solution was added. The solution was stirred for 10–60 minutes up to support dissolution. Simultaneously, the 100 mL Schlenk flask (flame-dried under vacuum) was charged by heptane (typically 20 mL) (and octadec-1-ene in the case of its polymerization) and left under agitation. Appropriate part of the support–activator solution was withdrawn from the Schlenk flask and added dropwise into the flask with stirring solvent to achieve the desired final support concentration (0.5–2 mg mL<sup>-1</sup>). The solution was stirred for 30–60 min and then the temperature was set to the desired polymerization temperature.

#### **Polymerization procedures**

Polymerization of ethylene was carried out in a 150 mL ovalshaped Schlenk flask equipped with a magnetic stirrer. The flask was annealed by a naked flame and purified by a vacuum-N<sub>2</sub> technique. The solvent, support and MAO were introduced into the flask according the protocol **P1** or **P2**. The flask with reagents was immersed into the ethanol bath and kept at the desired temperature for 10–20 min and then purged for 10 min by an ethylene flow. Polymerization was initiated by fast injection of the catalyst solution. After the desired time the polymerization mixture was quenched by pouring into 400 mL of methanol or ethanol acidified by 5 mL of HCl (36%). Resulting polyethylene was dried under vacuum at 60 °C for 24–48 h.

Polymerizations of octadec-1-ene were carried out in a 150 mL oval-shaped Schlenk flask equipped with a magnetic stirrer. The flask was annealed by a naked flame and purified by the N<sub>2</sub>-vacuum technique. Solvent, octadec-1-ene, support and MAO were introduced into the flask according to the respective protocol. The flask was immersed into the bath and kept at the desired temperature for 10–20 min. Polymerization was initiated by fast injection of the catalyst solution. The polymer solution was quenched into 400 mL of methanol or ethanol acidified by 5 mL of HCl (36%). Resulting poly(octadec-1-ene) was dried under vacuum at room temperature for 48–72 h.

#### Analysis

<sup>1</sup>H NMR spectra were recorded using a Bruker AC-400 NMR spectrometer using CDCl<sub>3</sub> at room temperature. <sup>1</sup>H NMR spectra of PE and polyoctadecene samples were determined on a 500 MHz Bruker Avance DRX 500 spectrometer in 1,2,4-tri-chlorobenzene/C<sub>6</sub>D<sub>6</sub> (90/10 v/v) solutions (10 mg mL<sup>-1</sup>) at 120 °C. Relaxation delay D1 was 10 s at 90° pulse angle.

The total number of branches per 1000 carbon atoms (N) was determined by integrating methyl proton signals with respect to signals of all protons in 'H NMR spectra and calculated using the formula:

$$N = \frac{2(I_{\rm CH_3})}{3(I_{\rm CH} + I_{\rm CH_3} + I_{\rm CH_3})} \times 1000$$
(1)

The crystallinity and melting point of PE were determined by DSC Q100 TA Instruments using a heating rate of 10 °C min<sup>-1</sup>. Crystallinity and melting point of PEs were determined from 1<sup>st</sup> run analysis using  $dH_m = 296$  J g<sup>-1</sup> for 100% crystalline PE.

Size exclusion chromatography (SEC) of polybutadiene samples was performed in THF at 30 °C at a flow rate of 1 mL min<sup>-1</sup> using a differential refractometer (Varian) and a multiangle light scattering photometer DAWN-EOS (Wyatt Technology) operating at 690 nm and a viscosimetric detector Viscostar-II (Wyatt). A refractive index increment (dn/dc) of 0.130 mL g<sup>-1</sup> was used for polybutadiene samples.<sup>23</sup> Four TSK columns (G5000HXL (9 µm), G4000HXL (6 µm), G3000HXL (6 µm), and G2000HXL (5 µm)) were used for separation.

The PE absolute values of weight average molar mass  $(M_w)$  and molar mass distribution  $(M_w/M_n)$  were determined using a Waters GPCV2000 instrument, equipped with two PL gel (300 × 7.5 mm) columns, and an online viscometer and a refractive index detector, at 150 °C in 1,2,4-trichlorobenzene at a flow rate of 0.9 mL min<sup>-1</sup>.

The morphology of final PE was observed by scanning electronic microscopy (SEM) on a JEOL JSM 2500 apparatus. For interpretation of SEM images, the qualitative scale was used:

Type of morphology:

GOOD-separated particles with a regular size.

GOOD/PARTIAL—particles of regular size, mostly separated, some of them connected with fibres.

PARTIAL—particles connected with fibres, formation of clusters.

PARTIAL/BAD—cauliflower-like structures.

BAD—no morphology observed.

Dynamic light scattering (DLS) measurements were performed using an ALV Laser goniometer, which consists of a 22 mW He Ne linear polarized laser with a 632.8 nm wavelength and an ALV-5000/EPP multiple tau digital correlator with 125 ns initial sampling time. The samples were kept at a constant temperature of 10 °C or 25 °C. The dispersions were introduced into 10 mm diameter glass cells and analyzed at the angle range of 40–130°.

Dynamic light scattering measurements were evaluated by fitting the measured normalized time autocorrelation function of the scattered light intensity with the help of the constrained regularization algorithm (CONTIN), which provides the distribution of relaxation times  $\tau$ ,  $A(\tau)$ , as the inverse Laplace transform of the  $g^{(1)}(t)$  function:

$$g^{(t)}(t) = \int_{0}^{x} A(\tau) \exp\left(-\frac{t}{T}\right) \mathrm{d}t \tag{2}$$

The apparent diffusion coefficient *D* was obtained by plotting the relaxation frequency,  $\Gamma$  ( $\Gamma = \tau^{-1}$ ), versus  $q^2$  where q is the wave vector defined as

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \tag{3}$$

and  $\lambda$  is the wavelength of the incident laser beam (632.8 nm),  $\theta$  is the scattering angle, and *n* is the refractive index of the media. The diffusion coefficient was then determined by extrapolation to zero concentration, and the hydrodynamic radius (*R*<sub>H</sub>) was calculated from the Stokes–Einstein relation

$$R_{\rm H} = \frac{k_{\rm B}T}{6\pi\eta\Gamma}q^2 = \frac{k_{\rm B}T}{6\pi\eta D_{\rm real}} \tag{4}$$

where  $k_{\rm B}$  is the Boltzmann constant,  $\Gamma$  is the relaxation frequency, T is the temperature, and  $\eta$  is the viscosity of the medium.

Dispersions used for the light scattering were prepared using protocols described above. Heptane and toluene were filtered through a 0.1  $\mu$ m PTFE membrane. MAO was filtered through a 0.45  $\mu$ m PTFE membrane.

#### Conclusions

In this paper, a new type of end-functionalized support for ethylene polymerization was synthesized. Commercially available hydroxyl-terminated cis-1,4-polybutadiene was modified to (di)carboxylic functions in order to increase the ability of polymer chains to self-assemble. Formation of micellar aggregates was confirmed by DLS in the presence of MAO. The concept of polymerization inside micelles was tested in ethylene polymerization with  $\alpha$ -diimine nickel catalyst. SEM microscopy proved significant improvement of morphology in the presence of these supports demonstrated by formation of spherical micrometric PE beads. Moreover, an increase of PE crystallinity in the presence of polybutadiene supports was observed and confirmed by <sup>1</sup>H NMR measurement. Micrometric particles were also prepared in  $\alpha$ -diimine nickel catalyzed ethylene polymerization in the presence of PI-b-PMMA supports. TMA and TMA/benzoic acid based cocatalysts were investigated in combination with  $\alpha$ -diimine catalysts. These catalytic systems can be used at low Al/Ni ratios, however, the morphology of gained PEs is less controlled. In the case of octadec-1-ene polymerization, the resulting polymer morphology was not influenced in the presence of the support and no polymer beads were formed.

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## Preparation of titanocene and zirconocene dichlorides bearing bulky 1,4-dimethyl-2,3-diphenylcyclopentadienyl ligand and their behavior in polymerization of ethylene

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#### 1. Introduction

# Highly substituted cyclopentadienes as ligands for group 4 metallocene complexes are still one of the important subjects of organometallic chemistry. Apart from complexes bearing persubstituted bulky cyclopentadienes [1], which were extensively studied in past decades, examples of complexes with relatively bulky phenyl substituted cyclopentadienyl rings still remain rather rare.

Complexes containing the substituted cyclopentadienyl ligand of general formula  $(1,2-Ph_2-4-R-C_5H_2)$  became exploited after the first zirconocene dichlorides with R = H in their ligands were developed [2]. Molecular orbitals of  $[\eta^5-(1,2-Ph_2-4-R-C_5H_2)_2ZrCl_2]$  (where R = H, Me, Ph) were calculated by DFT method and the theoretical and experimental UV spectra were compared [3]. Monocyclopentadienyl titanium trichlorides with the ligand 1,2-Ph\_2-4-R-C\_5H\_2 (where R = Me, Bu, Ph) after activation with MAO (MAO – methylaluminoxane) afforded syndiotactic polystyrene with high productivity and selectivity [4,5]. Very recently, the constrained geometry complex  $[\eta^5-(1,2-Ph_2-C_5H_3)(SiMe_2N-tBu)-TiMe_2]$  developed by Arriola et al. showed a high activity in

#### ABSTRACT

New metallocene dichlorides [ $\eta^5$ -(1,4-Me<sub>2</sub>-2,3-Ph<sub>2</sub>-C<sub>5</sub>H)<sub>2</sub>TiCl<sub>2</sub>] (**2**), [ $\eta^5$ -(1,4-Me<sub>2</sub>-2,3-Ph<sub>2</sub>-C<sub>5</sub>H)<sub>2</sub>ZrCl<sub>2</sub>] (**3**) and [ $\eta^5$ -(1,4-Me<sub>2</sub>-2,3-Ph<sub>2</sub>-C<sub>5</sub>H) $\eta^5$ -(C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>2</sub>] (**4**) were prepared from lithium salt of 1,4-dimethyl-2,3-diphenylcyclopentadiene (**1**) and [TiCl<sub>3</sub>(THF)<sub>3</sub>], [ZrCl<sub>4</sub>] and [ $\eta^5$ -(C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>3</sub>(DME)], respectively. Compounds **2–4** were characterized by NMR spectroscopy, EI-MS and IR spectroscopy, and the solid state structure of **3** was determined by single crystal X-ray crystallography. The catalytic systems **3**/MAO and **4**/MAO were almost inactive in polymerization of ethylene at 30–50 °C, however, they exhibited high activity at temperature 80 °C. The catalyst formed from **2** and excess of MAO was practically inactive at all temperatures.

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ethylene-styrene copolymerization with substantially increased ratio of styrene units in the resulting resin compared to other catalytic systems [6].

Coming from our permanent interest in group 4 metallocene dichlorides bearing phenyl substituted cyclopentadienyl ligand [7] we have investigated the cyclopentadienyl ligand having two methyl groups in 1,4- positions in addition to two vicinal phenyl groups (i.e. 1,4-Me<sub>2</sub>-2,3-Ph<sub>2</sub>-C<sub>5</sub>H). Although the parent 1,4-dimethyl-2,3-diphenylcyclopentadiene is known for more than 40 years, its utilization as a ligand in organometallic chemistry has been so far limited to only one example [8,9].

Here, we report the preparation and characterization of titanium and zirconium complexes containing 1,4-dimethyl-2,3-diphenylcyclopentadienyl ligand and the catalytic behavior of catalysts prepared thereof in polymerization of ethylene.

#### 2. Experimental

#### 2.1. Materials and equipments

All reactions with moisture- and air-sensitive compounds were carried out under argon (99.999%) or nitrogen (Siad 99.999%) atmosphere using standard Schlenk techniques. Solvents were dried, and freshly distilled prior to use.  $ZrCl_4$  and *n*-butyllithium (1.6 M) were obtained from Aldrich and used as received.

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 $[TiCl_3(THF)_3]$  [10] (THF – tetrahydrofuran) and  $[\eta^5-(C_5H_5)ZrCl_3-(DME)]$  [11] (DME – dimethoxyethane) were prepared according to literature procedures.

Ethylene (Siad 99.5%) for polymerization experiments was purified by passing through columns with copper catalyst and molecular sieves to remove traces of oxygen and moisture. Metallocene precatalysts were used as toluene solutions, which were stored in Schlenk vessels at 5 °C. MAO (Crompton, 10% in toluene) was used as received.

1,4-Dimethyl-2,3-diphenylcyclopentadiene was prepared following a published procedure and characterized by spectroscopic data which were missing in [8]. <sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz) were measured on a Bruker DRX500 spectrometer in C<sub>6</sub>D<sub>6</sub> or CDCl<sub>3</sub> solution at 300 K. Chemical shifts are given relative to the solvent signal ( $\delta_{\rm H}$  7.15 ppm,  $\delta_{\rm C}$  128.00 ppm for C<sub>6</sub>D<sub>6</sub> and  $\delta_{\rm H}$  7.26 ppm,  $\delta_{\rm C}$  77.16 ppm for CDCl<sub>3</sub>). Mass spectra were measured on a KRATOS concept IS instrument (Centre de Spectroscopie Moléculaire de l'Université de Bourgogne) at 70 eV. Infrared spectra were recorded on a Nicolet Avatar FT IR spectrometer in the range 400–4000 cm<sup>-1</sup>. Melting points of organic compounds and complexes were measured on Koffler block and were uncorrected. Elemental analyses (EA) were carried out on an Elementar vario EL III facility (Elementar) and average values from at least two measurements were taken. The polyethylene melting temperature was determined by DSC (TA Instruments, Q100) from the second heating run using heating and cooling rate 10 °C min<sup>-1</sup>. Molar masses of polyethylenes were determined by viscometry in decaline at 135 °C using Mark-Houwink parameters  $K = 6.2 \times 10^{-4}$ and *a* = 0.70 [12].

## *2.2.* Characterization of 1,4-dimethyl-2,3-diphenylcyclopenta-1,3-diene (1) [8]

<sup>1</sup>*H* NMR ( $C_6D_6$ ): 1.94 (s, 6H, Me); 2.74 (s, 2H, CH<sub>2</sub>), 6.97–7.01 (m, 2H, CH<sub>para</sub>, Ph), 7.05–7.12 (m, 8H, CH, Ph). <sup>13</sup>C{<sup>1</sup>H}( $C_6D_6$ ): 14.43 (Me); 49.90 (CH<sub>2</sub>); 126.37, 128.02, 129.92 (CH, Ph); 136.19, 137.24, 142.19 ( $C_q$ ;  $C_5Me_2Ph_2$  and Ph). EI-MS (70 °C): m/z (relative abundance) 247 (25), 246 (M<sup>+</sup>; 100), 231 ([M–Me]<sup>+</sup>; 16), 216 ([M–2Me]<sup>+</sup>; 14), 215 (22), 202 (9), 165 (5), 155 (6), 153 (6), 152 (6), 128 (4), 115 (6), 91 (3), 77 (2). IR (KBr, cm<sup>-1</sup>): 3100 (vw), 3076 (w), 3050 (m), 3028 (w), 2980 (w), 2969 (w), 2939 (w), 2902 (s), 2849 (m), 2731 (vw), 1955 (vw), 1888 (vw), 1816 (vw), 1767 (vw), 1602 (s), 1570 (w), 1494 (s), 1484 (m), 1440 (vs), 1373 (s), 1308 (w), 1240 (w), 1228 (vw), 1179 (vw), 1154 (w), 1128 (vw), 1076 (m), 1031 (vw), 1014 (vw), 1004 (w), 983 (m), 923 (w), 834 (vw), 772 (s), 756 (vs), 707 (vs), 683 (w), 646 (w), 620 (vw), 567 (m), 501 (vw), 433 (vw).

#### 2.3. Preparation of bis( $\eta^5$ -1,4-dimethyl-2,3-diphenylcyclopentadienyl)titanocene dichloride (**2**)

A 1.6 M *n*-butyllithium in hexane (4.5 ml, 7.19 mmol) was added dropwise to a solution of **1** (1.77 g, 7.19 mmol) in diethyl ether (80 ml) cooled to 0 °C. The reaction mixture was allowed to warm to room temperature and then stirred overnight. The resulting pale beige precipitate was filtered, washed three times with 20 ml of diethyl ether and dried in vacuum. A beige powder of lithium salt of **1** (1.65 g, 6.54 mmol) was dissolved in THF to give a the deep red solution. This was cooled to -78 °C, and  $[TiCl_3(THF)_3]$  (1.21 g, 3.27 mmol) was gradually added under stirring. The reaction mixture was allowed to warm to room temperature, and then refluxed for 12 h. The resulting dark green mixture was cooled to room temperature, and carbon tetrachloride (2.0 ml) was added. This caused an immediate color change to deep brown. After reflux for 2 h, all volatiles were evaporated to vacuum, the solid residue

was dissolved in 60 ml of toluene, and filtered through cellite pad. The volume of a dark brown toluene extract was concentrated to ca. 15 ml and stored at -18 °C for several days. Dark brown microcrystals were isolated, washed with cold toluene (5 ml), hexane (3 × 10 ml) and dried in vacuum. Yield 1.12 g (56%).

M.p. 235 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 2.06 (s, 6H, Me); 2.10 (s, 1.5H, PhMe)<sup>\*</sup>; 5.77 (s, 1H, CH, C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H); 6.93–6.98 (m, 2H, CH<sub>para</sub>, *Ph*); 6.99–7.02 (m, 1.5H, *Ph*Me)<sup>\*</sup>; 7.03–7.07 (m, 4H, *CH*<sub>ortho</sub>, *Ph*); 7.10–7.15 (m, 1H, PhMe)<sup>\*</sup>; 7.42–7.47 (m, 4H, CH<sub>meta</sub>, Ph). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 2.38 (s, 6H, Me); 2.43 (s, 1.5H, PhMe)\*; 6.41 (s, 1H, CH,  $C_5Me_2Ph_2H$ ; 7.22–7.36 (m, 10H + 2.5H<sup>\*</sup>, CH,  $C_5Ph$  and  $PhMe^*$ ). <sup>13</sup>C  ${}^{1}H$  (CDCl<sub>3</sub>): 17.15 (C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>); 21.61 (PhMe)<sup>\*</sup>; 116.98 (CH, C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H); 125.44, 128.37, 129.18 (*C*H, *Ph*Me)<sup>\*</sup>; 127.30, 127.40, 132.08 (CH, C<sub>5</sub>Ph); 125.25, 134.12, 139.27 (C<sub>q</sub>; C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H and *Ph*) 138.02 ( $C_q$ ; *Ph*Me)<sup>\*</sup>. Signals denoted by asterisk belong to half equivalent of solvating toluene. EI-MS (200 °C): m/z (relative abundance) 610 (12), 609 (8), 608 (M<sup>+</sup>; 17), 573 ([M-Cl]<sup>+</sup>; 47), 400 (10), 399 (8), 365 (78), 364 (33), 363 ([M-C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H]<sup>+</sup>; 100), 328 ([M-C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H-Cl]<sup>+</sup>; 22), 327 (21), 326 (14), 325 (27), 246 (62), 245 ([C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H]<sup>+</sup>; 88), 230 ([C<sub>5</sub>MePh<sub>2</sub>H]<sup>+</sup>; 27), 229 (35), 228 (25), 215 ([C<sub>5</sub>Ph<sub>2</sub>H]<sup>+</sup>; 49), 167 (14), 165 (12), 152 (11), 129 (7), 128 (5), 115 (9), 91 (22). IR (KBr, cm<sup>-1</sup>): 3087 (m), 3055 (s), 3026 (s), 2957 (m), 2917 (s), 1601 (m), 1575 (w), 1505 (w), 1494 (m), 1486 (m), 1463 (s), 1439 (s), 1422 (m), 1381 (m), 1366 (m), 1324 (vw), 1283 (vw), 1237 (vw), 1183 (w), 1156 (vw), 1079 (w), 1019 (m), 1002 (vw), 981 (vw), 919 (vw), 868 (w), 767 (s), 753 (vs), 731 (s), 698 (vs), 644 (w), 624 (m), 613 (w), 572 (vw), 506 (w), 465 (w). EA for C<sub>38</sub>H<sub>34</sub>Cl<sub>2</sub>Ti · 1/2 C<sub>7</sub>H<sub>8</sub> (655.55) calcd. C 76.04, H 5.84%; found C 75.49, H 5.95%.

#### 2.4. Preparation of bis( $\eta^5$ -1,4-dimethyl-2,3-diphenylcyclopentadienyl)zirconocene dichloride (**3**)

A 1.6 M *n*-butyllithium in hexane (13.4 ml, 21.4 mmol) was added dropwise to a stirred solution of **1** (5.27 g, 21.4 mmol) in toluene (60 ml). The reaction mixture with the precipitated lithium salt of **1** was stirred for 5 h, and  $ZrCl_4$  (2.50 g, 10.7 mmol) was added in one portion. The resulting suspension was stirred for 1 h at ambient temperature and then refluxed for 2 days. The volatiles were evaporated and the residue was heated to 170 °C in vacuum for 4 h to remove traces of unreacted **1**. The resulting yellow-brown solid was extracted in Soxhlet extractor with boiling hexane within 2 days. The yellow solid which precipitated during extraction from the hexane solution was isolated, washed with hexane (3 × 15 ml), ethanol (3 × 15 ml), and dried in vacuum. Yield 2.06 g (30%).

M.p. 264 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 2.10 (s, 6H, Me); 5.69 (s, 1H, CH, C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H); 6.91–6.98 (m, 2H, CH<sub>para</sub>, Ph); 7.01–7.09 (m, 4H, CHortho, Ph); 7.40-7.45 (m, 4H, CH<sub>meta</sub>, Ph). <sup>13</sup>C{<sup>1</sup>H}(C<sub>6</sub>D<sub>6</sub>): 16.05 (*Me*); 114.02 (CH, C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H); 127.35, 127.88, 132.06 (CH, *Ph*); 122.01, 134.31, 134.43 (*C*<sub>q</sub>; *C*<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H and *Ph*). EI-MS (210 °C): *m*/*z* (relative abundance) 654 (9), 653 (6), 652 (M<sup>+</sup>; 11), 651 (7), 650 (10), 411 (50), 410 (25), 409 (97), 408 (51), 407  $([M-C_5Me_2Ph_2H]^+; 100), 406 (61), 405 (99), 393 (16), 392 (8),$ 391 (23), 390 (15), 389 (31), 373 (28), 371 (19), 370 (12), 369 (30), 368 (12), 367 (24), 365 (12), 246 (39), 245 ([C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H]<sup>+</sup>; 18), 244 (14), 230 ([C<sub>5</sub>MePh<sub>2</sub>H]<sup>+</sup>; 14), 229 (28), 228 (20), 216 (13), 215 ([C<sub>5</sub>Ph<sub>2</sub>H]<sup>+</sup>; 27), 167 (11), 165 (13), 152 (12), 115 (16), 91 (19), 77 (10). IR (KBr, cm<sup>-1</sup>): 3089 (m), 3051 (m), 2988 (w), 2955 (m), 2923 (m), 1601 (m), 1576 (w), 1506 (m), 1485 (w), 1462 (m), 1441 (s), 1381 (w), 1322 (vw), 1311 (vw), 1283 (vw), 1238 (vw), 1184 (w), 1157 (vw), 1079 (w), 1032 (w), 1017 (w), 1003 (vw), 983 (vw), 920 (vw), 863 (vw), 844 (m), 767 (s), 753 (vs), 699 (vs), 645 (w), 626 (m), 614 (w), 571 (w), 506 (vw), 416 (vw). EA for C<sub>38</sub>H<sub>34</sub>Cl<sub>2</sub>Zr (652.82) calcd. C 69.92, H 5.25%; found C 69.64, H 5.36%.

#### 2.5. Preparation of $(\eta^5$ -cyclopentadienyl) $(\eta^5$ -1,4-dimethyl-2,3diphenylcyclopentadienyl)zirconocene dichloride (**4**)

A mixture of solid lithium salt of **1** (prepared as for **2**) (0.36 g, 1.42 mmol) and  $[(\eta^5-C_5H_5)ZrCl_3(DME)]$  (0.50 g, 1.42 mmol) was cooled to -78 °C and 20 ml of toluene was added. The reaction mixture was stirred for 10 min at this temperature, then allowed to warm to room temperature, and refluxed for 2 days. The resulting greenish suspension was filtered through a cellite pad. The resulting yellow filtrate was concentrated to ca. 8 ml and stored in a freezer (-18 °C) for several days. Yellowish microcrystals were collected, washed with cold toluene (5 ml), hexane (3 × 5 ml), and dried in vacuum. Yield 0.26 g (39%).

M.p. 164–165 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 2.01 (s, 6H, Me); 5.42 (s, 1H, CH, C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H); 5.98 (s, 5H, CH, C<sub>5</sub>H<sub>5</sub>); 6.94–6.99 (m, 2H, CH<sub>para</sub>, Ph); 7.02-7.07 (m, 4H, CHortho, Ph); 7.30-7.34 (m, 4H, CHmeta, Ph).  $^{13}C{^{1}H}(C_6D_6)$ : 15.97 (*Me*); 115.22 (*CH*,  $C_5Me_2Ph_2H$ ); 116.51 (*CH*, C<sub>5</sub>H<sub>5</sub>); 127.40, 128.04, 131.54 (CH, Ph); 124.24, 131.49, 134.04 ( $C_a$ ;  $C_5$ Me<sub>2</sub>Ph<sub>2</sub>H and Ph). EI-MS (210 °C): m/z (relative abundance) 474 (20), 473 (12), 472 (M<sup>+</sup>; 28), 471 (14), 470 (27), 435 ([M-Cl]<sup>+</sup>; 5), 411 (33), 410 (18), 409 (71), 408 (36), 407 ([M-C<sub>5</sub>H<sub>5</sub>]<sup>+</sup>; 99), 406 (43), 405 (100), 391 (12), 389 (16), 371 (13), 369 (22), 367 (19), 365 (11), 246 (15), 245 ([C<sub>5</sub>Me<sub>2</sub>Ph<sub>2</sub>H]<sup>+</sup>; 8), 244 (9), 229 (21), 228 (17), 227  $([M-C_5Me_2Ph_2H]^+; 16)$ , 225 (16), 215 (22), 202 (11), 165 (11), 152 (11), 128 (11), 115 (14), 91 (15), 77 (11). IR (KBr, cm<sup>-1</sup>): 3112 (m), 3089 (m), 3060 (m), 2989 (w), 2956 (w), 2929 (w), 1601 (w), 1576 (vw), 1505 (w), 1485 (w), 1464 (w), 1441 (s), 1380 (w), 1314 (vw), 1239 (vw), 1185 (vw), 1157 (vw), 1127 (vw), 1077 (w), 1016 (m), 1003 (vw), 986 (vw), 919 (vw), 819 (vs), 766 (s), 754 (s), 701 (vs), 669 (w), 654 (w), 628 (w), 615 (w), 572 (w), 508 (w), 418 (w). EA for C<sub>24</sub>H<sub>22</sub>Cl<sub>2</sub>Zr (472.57) calcd. C 61.00, H 4.69%; found C 60.62, H 4.52%.

#### 2.6. X-ray crystallography

The yellow-green crystal of **3** was grown from its dichloromethane solution during hexane diffusion. Diffraction data were collected on a Nonius KappaCCD diffractometer. The structure was solved by direct methods (siR-97) [13] and refined by weighted full-matrix least-squares on  $F^2$  (shelxl-97) [14]. All non hydrogen

Table 1

Crystallographic data, data collection and structure refinement data for compound 3.ª

| Chemical formula   | C <sub>38</sub> H <sub>34</sub> Cl <sub>2</sub> Zr |
|--|--|
| Molecular weight   | 652.77   |
| Crystal system   | Monoclinic   |
| Space group  | <i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)        |
| Temperature (K)  | 150(2)   |
| a (Å)  | 21.7600(4)   |
| b (Å)  | 14.9530(3)   |
| <i>c</i> (Å)   | 19.2860(4)   |
| α (°)  | 90.000   |
| β (°)  | 91.8930(13)  |
| γ (°)  | 90.000   |
| Ζ  | 8  |
| Crystal size (mm <sup>3</sup> )                          | $0.50\times0.05\times0.05$                         |
| $D_{\text{calc}} \left( g \times \text{cm}^{-3} \right)$ | 1.383  |
| $\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )               | 0.546  |
| F(000)   | 2688   |
| θ range (°)  | 1.72-26.73   |
| hkl range  | -27/27, -15/18, -24/24                             |
| Reflections collected/unique                             | 46774/13245  |
| Parameters   | 747  |
| $R, wR [I > 2\sigma(I)]$                                 | 0.0403, 0.0727                                     |
| R, wR (all data)   | 0.0761, 0.0842                                     |
| S  | 1.011  |
| $\Delta  ho_{ m max,min} ({ m e}{ m \AA}^{-3})$          | 0.362, -0.576                                      |

<sup>a</sup>  $R(F) = \Sigma ||F_0| - |F_c||/\Sigma |F_0|, wR(F_2) = [\sum (w(F_0^2 - F_c^2)^2)/(\sum w(F_0^2)^2)]^{1/2}, S = [\sum (w(F_0^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}.$ 

atoms were refined with anisotropic thermal motion parameters. The hydrogen atoms were included in calculated positions. Relevant crystallographic data are collected in Table 1.

#### 2.7. Ethylene polymerization

Polymerizations were carried out in 100 ml magnetically stirred jacket glass reactor. Toluene, ethylene and MAO solution were dosed in this order and the mixture was stirred for 15 min to equilibrate reaction temperature. The polymerization was started by injection of the precatalyst solution. The ethylene pressure was kept constant (1.1 atm) during the whole polymerization. The polymerization was quenched by 2 ml of EtOH/HCl mixture and polymer precipitated in a large excess of 3% HCl solution in EtOH. The polymer was filtered and dried in vacuum to constant weight.

#### 3. Results and discussion

#### 3.1. Preparation of 1,4-dimethyl-2,3-diphenylcyclopentadiene (1)

Compound **1** was prepared according to a reported synthetic procedure (Scheme 1) [8]. Although direct preparation of trans-2,5-dimethyl-3,4-diphenylcyclopent-2-en-1-one (as the key intermediate) by condensation of 3-pentanone with 2 equivalents of benzaldehyde catalyzed by  $ZrOCl_2 \cdot 8H_2O$  was reported, the published conditions were compatible rather with a microscale preparation [15]. Recently it has been observed that replacement of ZrOCl<sub>2</sub> · 8H<sub>2</sub>O catalyst by [TiCl<sub>4</sub>(THF)<sub>2</sub>] leads to higher yields and the reaction scale can be enlarged to a multigram quantity [16]. Nevertheless, the use of inert conditions still makes the reaction quite difficult. Thus, we preferred base-catalyzed condensation of 3-pentanone with benzil [17–19], followed by repeated reduction and acid-catalyzed dehydration providing **1** as a yellow crystalline solid (Scheme 1). In dependence on the conditions of the last dehydration step we obtained the desired product as cyclopentadiene with  $C_{2v}$  symmetry or as a mixture of isomers. The cyclopentadiene 1 has very similar EI-MS pattern to previously prepared substitution isomer 2,3-dimethyl-1,4-diphenylcyclopentadiene (I) [7]. Both compounds have the molecular ion m/z 246 as a base peak, whereas the abundance of other ions is rather low. On the other hand <sup>1</sup>H NMR of C<sub>6</sub>D<sub>6</sub> solutions of the compounds are quite different showing remarkable redistribution of electron density as a consequence of different position of methyl and phenyl groups in 1 and I. As the most remarkable was a significant downfield shift of methylene protons in 1 compared to I (2.74 ppm in 1, 3.47 ppm in I; for comparison: 1,2,3,4-tetramethylcyclopentadiene in CDCl<sub>3</sub> 2.60 ppm [20], 1,2,3,4-tetraphenylcyclopentadiene in  $C_6D_6$  3.72 ppm [21]). The similar downfield shift was observed for all aromatic protons in 1 with respect to I. A lower stability



Scheme 1. Synthesis of 1,4-dimethyl-2,3-diphenylcyclopentadiene (1) as published in Ref. [8].

of **1** compared to **I** is to be noticed, since prolonged storage at room temperature led to the compound decomposition. We suggest that this behavior results from a lower extent of conjugation of cyclopentadiene and phenyl rings in **1**.

#### 3.2. Preparation of group 4 metallocene dichlorides

Synthetic procedure for preparation of metallocene dichlorides **2–4** is depicted in Scheme 2. Deprotonation of ligand precursor **1** with *n*-butyllithium in diethyl ether affords lithium salt in almost quantitative yield. The reaction of two equivalents of the lithium salt with  $[TiCl_3(THF)_3]$  in THF gives a titanocene chloride, whose oxidation with an excess of CCl<sub>4</sub> yields titanocene dichloride **2** in moderate yield. The complex **2** crystallizes from toluene solution as hemisolvate with toluene as was detected by NMR spectroscopy and elementary analysis. The zirconocene dichloride **3** was prepared in modest yield by the reaction of ZrCl<sub>4</sub> with two equivalents of the lithium salt of ligand **1** in boiling toluene.



Scheme 2. Preparation of complexes 2-4.

For synthesis of complex **4** bearing different cyclopentadienyl ligands two synthetic pathways were attempted. Initially, a consecutive addition of the lithium salt of **1** and cyclopentadienyllithium to ZrCl<sub>4</sub> was performed. The NMR characterization of crude product revealed a mixture of **4**, **3** and  $[\eta^{5}-(C_{5}H_{5})_{2}ZrCl_{2}]$  in ratio 78:8:14. Although **3** was removed from the mixture by fractional crystallization, **4** could not be obtained in pure form due to its similar solubility to that of  $[\eta^{5}-(C_{5}H_{5})_{2}ZrCl_{2}]$  (the final product still contained about 10% of  $[\eta^{5}-(C_{5}H_{5})_{2}ZrCl_{2}]$ ). Therefore the reaction of lithium salt of **1** with  $[\eta^{5}-(C_{5}H_{5})_{2}ZrCl_{3}]$  was used as an alternative reaction pathway. The later reaction led to zirconocene dichloride **4** as a sole product in moderate yield.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **2–4** showed the  $C_{2v}$  time averaged symmetry indicating free rotation of both cyclopentadienyl and phenyl rings at room temperature. All complexes displayed characteristic signals for methyl groups directly bonded to ring moiety with chemical shifts 2.06 ppm for **2**, 2.10 ppm for **3** and 2.01 ppm for **4**. The singlet signals belonging to the CH group of cyclopentadienyl ring appeared at 5.77 ppm for **2**, 5.69 ppm for **3** and 5.42 ppm for **4**.

EI-MS spectra of all complexes showed only low abundant molecular ions (m/z = 608 for **2**, m/z = 652 for **3** and m/z = 472 for **4**), while the most abundant fragment ion was  $[Cp'MCl_2]^+$ . All spectra showed a surprisingly abundant fragment m/z = 246 which could be assigned to a protonated form of ligand  $[Cp'H]^+$ , which is for **3** and **4** even more abundant then  $[Cp']^+$  (m/z = 245).

#### 3.3. Crystal structure analysis

The complex **3** crystallizes with two independent molecules (denoted **3a** and **3b**) in the unit cell (space group  $P_{2_1}/c$ ). Molecular structures of molecules **3a** and **3b** are shown in Fig. 1, selected bond lengths and angles for both independent molecules are given in Table 2. The zirconium atoms have distorted tetrahedral environment with the Zr–Cl distances 2.4247(6) Å and 2.4262(7) Å for **3a** and 2.4103(8) Å and 2.4326(8) Å for **3b** which is close to other octasubstituted zirconocene dichlorides (average Zr–Cl distance in [ZrCl<sub>2</sub>{ $\eta^{5}$ -( $C_{5}Me_{4}H$ )]<sub>2</sub>] is 2.434(3) Å [22], in [ZrCl<sub>2</sub>{ $\eta^{5}$ -( $C_{5}H-1,4$ -Ph<sub>2</sub>-2,3-Me<sub>2</sub>)]<sub>2</sub>] is 2.432(1) Å [7]). The dihedral angles between least-square planes of cyclopentadienyl rings are similar for both independent molecules (56.01(16)° in **3a** and 57.94(16)° in **3b**). The values are comparable to the value found in [ZrCl<sub>2</sub>{ $\eta^{5}$ -( $C_{5}H_{2}$ -1,2-Ph<sub>2</sub>-4-Me)}<sub>2</sub>] (56.8°) and substantially smaller than in corresponding nonmethylated analogue [ZrCl<sub>2</sub>{ $\eta^{5}$ -( $C_{5}H_{3}$ -1,



Fig. 1. Molecular structures of 3a and 3b (thermal ellipsoids are given with 30% probability). Hydrogen atoms are omitted for clarity.

| Table 2                                    |  |
|--|--|
| Selected bond lengths (Å) and angles (°) f | for molecules <b>3a</b> and <b>3b</b> . <sup>a</sup> |

| 3a                                 |                   |                                    |                   |
|------------------------------------|-------------------|------------------------------------|-------------------|
| Zr1–Cl1                            | 2.4247(6)         | Zr1-Cl2                            | 2.4262(7)         |
| $Zr1-C_g(1)^b$                     | 2.2498(12)        | $Zr1-C_g(2)^b$                     | 2.2507(11)        |
| Zr1-C <sub>ring</sub>              | 2.467(2)-2.624(2) |                                    |                   |
| C-C <sub>Cp ring</sub>             | 1.404(4)-1.437(4) | C-C <sub>Ph ring</sub>             | 1.365(5)-1.400(4) |
| $C_{ring}-C_{Ph}$                  | 1.479(4)-1.487(4) | C <sub>ring</sub> -C <sub>Me</sub> | 1.503(4)-1.511(4) |
| Cl1-Zr1-Cl2                        | 96.81(3)          | $C_g(1)$ – $Zr1$ – $C_g(2)^b$      | 130.21(4)         |
| $\varphi^{c}$                      | 56.01(16)         | $\tau^{d}$                         | 56.35(4)          |
| 3b                                 |                   |                                    |                   |
| Zr2-Cl3                            | 2.4326(8)         | Zr2-Cl4                            | 2.4103(8)         |
| $Zr2-C_g(3)^b$                     | 2.2432(13)        | $Zr2-C_g(4)^b$                     | 2.2495(12)        |
| Zr2-Cring                          | 2.468(3)-2.637(2) |                                    |                   |
| C-C <sub>Cp ring</sub>             | 1.399(4)-1.433(4) | C-C <sub>Ph ring</sub>             | 1.363(6)-1.400(4) |
| C <sub>ring</sub> -C <sub>Ph</sub> | 1.478(4)-1.485(4) | C <sub>ring</sub> -C <sub>Me</sub> | 1.504(4)-1.508(4) |
| Cl3-Zr2-Cl4                        | 94.60(3)          | $C_{g}(3) - Zr2 - C_{g}(4)^{b}$    | 129.19(5)         |
| $\varphi^{c}$                      | 57.94(16)         | $	au^{d}$                          | 44.19(5)          |

<sup>a</sup>Extreme values in the two independent molecules **3a**, **3b** of the unit cell, the cyclopentadienyl ring atoms are denoted C101–C105 and C120–C124 for **3a**, and C201–C205 and C220–C224 for **3b** as shown in Fig. 1.

 $^{\rm b}$  Cg(1), Cg(2), Cg(3) and Cg(4) are centroids of the C(101-105), C(120-124), C(201-205) and C(220-224) cyclopentadienyl rings.

<sup>c</sup> Dihedral angle between the least-squares planes of the cyclopentadienyl rings.

<sup>d</sup> Torsion angles C(105)-Cg(1)-Cg(2)-C(124) and C(205)-Cg(3)-Cg(4)-C(224).

2-Ph<sub>2</sub>)]<sub>2</sub>] (61.6°, 62.3°) [2]. Similarly the Cg–Zr–Cg angle value increases in the opposite order [ZrCl<sub>2</sub>{ $\eta^{5}$ -(C<sub>5</sub>H<sub>3</sub>-1,2-Ph<sub>2</sub>)]<sub>2</sub>] (126.6° and 126.9°) [ZrCl<sub>2</sub>{ $\eta^{5}$ -(C<sub>5</sub>H<sub>2</sub>-1,2-Ph<sub>2</sub>-4-Me)]<sub>2</sub>] (129.5°) and **3** (130.21(4)° and 129.19(15)°). The both data reflect an increased crowding of open side of molecules with increasing number of methyl groups at the cyclopentadienyl rings. The cyclopentadienyl rings in **3a** and **3b** are staggered. There mutual rotation, however, differs as indicated by torsion angles C(105)–Cg(1)–Cg(2)–C(124) 56.35° for **3a** and C(205)–Cg(3)–Cg(4)–C(224) 44.19° for **3b**. All phenyl groups are rotated away from coplanar conformation with cyclopentadienyl moiety, the dihedral angles between least-square planes of Cp' and Ph rings ranging 38.09(16)–55.16(14)°. This diminishes the conjugation of both aromatic systems.

#### 3.4. Polymerization of ethylene

Complexes **2–4** (and [ZrCl<sub>2</sub>{ $\eta^{5}$ -(C<sub>5</sub>H<sub>5</sub>)}<sub>2</sub>] for comparison) were activated by excess MAO and evaluated in polymerization of ethylene (Table 3). The complexes **3** and **4** showed only negligible activity at 30–50 °C, whereas at 80 °C they both possessed high activity at almost the same level (370–390 kg<sub>PE</sub>/mol<sub>Met</sub>/h). The dramatic increase of activity by raising temperature from 50 °C to 80 °C could be attributed to a steric crowding of the active center by the bulky phenyl and methyl groups. The crowding of the active site then influenced either formation of cationic centre by cocatalyst or insertion of ethylene into Zr–C bond. The influence of steric crowding on activation of bulky [Zr{Me<sub>2</sub>Si( $\eta^{5}$ -C<sub>5</sub>Ph<sub>4</sub>)( $\eta^{5}$ -C<sub>5</sub>H<sub>3</sub>*t*-Bu)}] by MAO was recently elucidated by DFT calculation, which showed

#### Table 3

Comparison of 2-4/MAO activity in ethylene polymerization.

| Catalyst                               | Т<br>(°С) | t<br>(h) | $[M]\times 10^4M$ | m <sub>PE</sub><br>(g) | Activity<br>(kg <sub>PE</sub> /mol <sub>Met</sub> /h) | $M_{ m v}$<br>(kg mol <sup>-1</sup> ) | T <sub>m</sub><br>(°C) |
|--|-----------|----------|-------------------|------------------------|---|---------------------------------------|------------------------|
| <b>2</b> /MAO                          | 50        | 2        | 2.0               | 0.012                  | 1   |                                       |                        |
| <b>2</b> /MAO                          | 80        | 2        | 2.0               | 0.028                  | 1   |                                       |                        |
| <b>3</b> /MAO                          | 30        | 3        | 1.0               | 0.0002                 | 0   |                                       |                        |
| <b>3</b> /MAO                          | 50        | 12       | 2.0               | 0.017                  | 0   |                                       |                        |
| <b>3</b> /MAO                          | 80        | 1        | 1.0               | 1.939                  | 388   | 10.6                                  | 130.7                  |
| <b>4</b> /MAO                          | 50        | 2        | 2.0               | 0.032                  | 2   |                                       |                        |
| 4/MAO                                  | 80        | 1        | 1.0               | 1.845                  | 369   | 18.0                                  | 131.7                  |
| Cp <sub>2</sub> ZrCl <sub>2</sub> /MAO | 30        | 1        | 1.0               | 0.721                  | 144   |                                       |                        |
| Cp <sub>2</sub> ZrCl <sub>2</sub> /MAO | 80        | 1        | 1.0               | 3.748                  | 750   | 11.4                                  | 129.0                  |

Polymerization conditions: Al/M = 900 (M = Ti, Zr), toluene 50 ml, ethylene pressure 1.1 atm.

#### Table 4

The effect of catalyst/cocatalyst ratio on polymerization activity of zirconocene  $\mathbf{3}/\mathsf{MAO}$  system.

| Al/Zr | $[Zr]\times 10^4M$ | $m_{ m PE}$ (g) | Activity $(kg_{PE}/mol_{Met}/h)$ |
|-------|--------------------|-----------------|----------------------------------|
| 200   | 2.4                | 0.103           | 4                                |
| 500   | 1.8                | 1.089           | 61                               |
| 900   | 1.6                | 3.526           | 221                              |

Polymerization conditions: temperature 80 °C, polymerization time 2 h, toluene 50 ml, ethylene pressure 1.1 atm.

that the abstraction of a methyl group to form the cationic active species was endotermic (8.5 kcal/mol) [23]. Moreover, the DFT calculation showed that barrier for insertion of ethylene into Zr–Me bond is relatively high (12–24 kcal/mol for  $[Cp_2ZrMe]^+$ ) [24,25]. Therefore, an elevated temperature is crucial for the polymerization promoted by catalysts derived from bulky **3** or **4**.

About half value of activity of complexes **3** and **4** in comparison with the standard  $[ZrCl_2\{\eta^5-(C_5H_5)\}_2]$  at 80 °C can be attributed to a lower concentration of cationic active species during polymerization, because the electron-attracting phenyl substituents on cyclopentadienyl rings are known to destabilize the cationic center [26]. A low stability of cationic species is in line with the observed decrease in activity with lowering of the Al/Zr ratio at 80 °C (Table 4). However, it should be noted that is a general trend for most metallocene catalysts [27,28].

Molar masses of polyethylenes prepared using 3, 4 and  $[ZrCl_2{\eta^5-(C_5H_5)}_2]$  under given experimental conditions (Table 3) are in the range 10000–18000 g mol<sup>-1</sup>. These relatively low values are due to a low ethylene pressure, high reaction temperature (necessary for a reasonable propagation rate) and rather high catalyst concentration, all factors enabling  $\beta$ -H elimination and chain-transfer to aluminium as observed previously in  $[ZrCl_2{\eta^5} (C_5H_5)_2$ ]/MAO catalyzed ethylene polymerization under similar conditions [29,30], the molar mass of polyethylene obtained with bulky complex **3**, for which the lower extent of  $\beta$ -H elimination could be expected, is surprisingly similar to molar mass of the polymer produced by the standard  $[ZrCl_2{\eta^5-(C_5H_5)}_2]$  catalysts. In contrast, the highest molar mass polyethylene was obtained by less sterically hindered complex 4. This shows the complexity of polymerization process in which the simultaneous propagation and chain-transfer reactions take place and their proportion determines final chain length. The melting transition temperatures of prepared polyethylene matrices (129.0–131.7 °C) are in range typical for linear polyethylene, about 10 °C lower than in the case of  $[ZrCl_2{\eta^5-(C_5H_3-1,2-Ph_2)}_2]/MAO$  catalyst [2]. This difference arise from different conditions for polymerization used in [2] (low temperature, high ethylene pressure, lower catalyst concentration) where chain-transfer reactions were significantly suppressed and polyethylenes with very high molar masses were prepared.

Contrary to catalysts derived from zirconocene dichlorides **3** and **4**, the catalyst formed from mixing **2** with MAO is practically inactive at any temperature. The same behavior was found in  $[TiCl_{2}{\eta^{5}-(C_{5}H-1,4-Ph_{2}-2,3-Me_{2})}_{2}]/MAO$  system [7]. We suggested the behavior as a consequence of the reduction of a titanium cationic center to catalytically inactive Ti(III) center induced by MAO and/or trimethylaluminum (inherent part of MAO solutions). An easier reduction of titanocene dichlorides compared to zirconocene dichlorides is well known and was evaluated by cyclic voltametry [31,32].

#### 4. Conclusions

Combination of phenyl and methyl groups in the cyclopentadienyl ligand framework has a specific impact on catalysts performance. The catalysts formed from combination of MAO with **3** or **4** required a high temperature and relatively high Al/Zr ratio to reach high ethylene polymerization activity. The determining factor is presumably the presence of electron-attracting bulky phenyl groups bonded to cyclopentadienyl moiety. A high tendency of titanium to reduction increased by the presence of electronattracting phenyl groups is probably responsible for negligible activity of the catalyst derived from **2** at all studied temperatures.

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#### **Appendix A. Supplementary material**

CCDC 679430 contains the supplementary crystallographic data for 3. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem. 2008.10.019.

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## Synthesis and catalytic activity of camphor titanium complexes

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#### ABSTRACT

Three new camphor-titanium complexes [TiClCp<sub>2</sub>L] (L = <sup>1</sup>L, (1); <sup>2</sup>L, (2) and <sup>3</sup>LH (3)) were obtained through replacement of one chloride by a camphor-type ligand (<sup>1</sup>LH, <sup>2</sup>LH, <sup>3</sup>LH<sub>2</sub> (3)) at the coordination sphere of [TiCl<sub>2</sub>Cp<sub>2</sub>]. Complexes **1** and **2** were structurally characterized by X-ray diffraction analysis showing that coordination occurs through the oxygen atom of the hydroxo group (1) with cooperative coordination of the nitrogen atom of the oxime complex in **2**. Upon activation with MAO complexes **1** and **2** promote ethylene polymerization and ethylene/norbornene co-polymerization while compound **3** displays no catalytic activity for either one or the other process. At 50 °C the catalytic activity complex of **2** (852 kg<sub>PE</sub> mol<sup>-1</sup>h<sup>-1</sup>) for ethylene polymerization is higher than that of compound **1** (668 kg<sub>PE</sub> mol<sup>-1</sup>h<sup>-1</sup>) which is similar to that of [TiCl<sub>2</sub>Cp<sub>2</sub>] (670 kg<sub>PE</sub> mol<sup>-1</sup>h<sup>-1</sup>). The catalytic activity of complex 1 displays a higher dependence on the temperature than that of compound **2** which is attributed to the strength of the Ti–O bond that renders generation of the active site more difficult in **1**. Compounds **1** and **2** are also active catalysts for co-polymerization of ethylene with norbornene affording copolymers with approximately 15 mol% of norbornene content.

The microstructures of the polyethylenes and ethylene norbornene co-polymers were checked by NMR and their melting points were measured by DSC.

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#### 1. Introduction

Within our search for catalysts that promote C–C or C–O bond formation we synthesized several camphor-derived Pd and Pt complexes that are efficient and selective catalysts for the activation of the triple bonds of alkynes or alkynols [1–3] towards cyclization.

We now report the synthesis of the first structurally characterized camphor titanium complexes [TiClCp<sub>2</sub>L] (L = <sup>1</sup>L, <sup>2</sup>L, Scheme 1) and the evaluation of their catalytic properties for CC double bond activation. The choice of the Ti core for coordination of the camphor-type species was based on the fact that [TiCl<sub>2</sub>Cp<sub>2</sub>] catalysis ethylene polymerization and several titanocene and half-titanocene complexes [TiCl<sub>2</sub>CpL] [4,5] are efficient catalysts for co-polymerization of ethylene with cyclic unsaturated substrates [6–8] and we wished to evaluate the effect of the camphor ligand (<sup>1</sup>LH, <sup>2</sup>LH and <sup>3</sup>LH<sub>2</sub>) in the activity of the Ti-site for ethylene polymerization and ethylene/norbornene co-polymerization processes as well as check for the characteristics of the polymers and co-polymers with respect to molecular weight (polyethylenes) and norbornene content (co-polymers).

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#### 2. Results and discussion

#### 2.1. Synthesis and characterization of complexes

The affinity of Ti(IV) for oxygen-donor ligands is well known, thus we decided to explore this characteristic to promote coordination of the camphor compounds <sup>1</sup>LH, <sup>2</sup>LH and <sup>3</sup>LH<sub>2</sub> (Scheme 1) to titanium. Under basic conditions the deprotonation of the hydroxy group of the camphor species promotes its coordination to titanium by replacement of one chloride ligand at [TiCl<sub>2</sub>Cp<sub>2</sub>].

We succeeded to prepare complexes [TiClCp<sub>2</sub>L] (L = <sup>1</sup>L, (1); <sup>2</sup>L, (2) and <sup>3</sup>LH (3)) using triethylamine as solvent. Compounds [TiClCp<sub>2</sub>(<sup>1</sup>L)] (1) and [TiClCp<sub>2</sub>(<sup>2</sup>L)] (2) were structurally characterized by X-ray diffraction analysis (Fig. 1). Data shows they crystallize in the  $P2_12_12_1$  space group with *pseudo*-octahedral geometry. Coordination of the camphor ligand in complex 2 involves the contribution of the oxygen and the nitrogen atoms of the oxime group, thus the ligand behaves as bidentate ( $\eta^2$ ). In both complexes the Cp rings occupy the centre of two triangular faces that share one equatorial edge; the chloride atom occupies one of the remaining equatorial positions and the other is occupied by the oxygen atom (1) or the oxime group (2).

Selected bond lengths and angles for complexes **1** and **2** are displayed in Table 1. In the structures a few aspects are worthwhile



**P**8

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Scheme 1. Camphor derived species used as ligands.



Fig. 1. ORTEP drawings showing labeling scheme for complexes 1 (left) and 2 (right).

| Table 1  |      |         |     |        |     |           |   |     |    |
|----------|------|---------|-----|--------|-----|-----------|---|-----|----|
| Selected | bond | lengths | and | angles | for | complexes | 1 | and | 2. |

| [TiClCp <sub>2</sub> ( <sup>1</sup> L)]<br>( <b>1</b> ) |           | [TiClCp <sub>2</sub> ( <sup>2</sup> L)] <sup>a</sup><br>( <b>2</b> ) |                    |
|---|-----------|--|--------------------|
| Bond lengths (Å)  |           |  |                    |
| Ti-Cl   | 2.405(2)  | Ti-Cl  | 2.481(2); 2.478(2) |
| Ti-O  | 1.824(5)  | Ti-O   | 2.053(1); 2.064(1) |
| 0-C11   | 1.419(9)  | Ti-N   | 2.076(2); 2.072(2) |
| Ti-Cp <sub>av</sub>                                     | 1.732     | Ti–Cp (av)   | 1.737              |
| C11-C16   | 1.560(11) | O-N  | 1.332(2); 1.329(2) |
| C16-N   | 1.459(10) | C34-N  | 1.276(2); 1.281(2) |
|   |           | C34-C43  | 1.495(3); 1.494(3) |
|   |           | C43-04   | 1.211(3); 1.219(2) |
| Bond angles (°)   |           |  |                    |
| Cl-Ti-O   | 93.4(2)   | Cl-Ti-O  | 78.2(5); 78.8(6)   |
| Ti-O-C  | 152.9(5)  | Cl-Ti-N  | 115.8(5); 116.2(6) |
| Cp–Ti–Cp  | 129.8     | O-Ti-N   | 37.6(5); 37.5(6)   |
|   |           | Ti-N-C   | 166.7(1); 165.7(1) |
|   |           | O-N-C  | 121.7(2); 123.4(2) |
|   |           | Cp–Ti–Cp   | 131.2; 130.2       |

<sup>a</sup> There are two molecules in the asymmetric unit.

to comment, e.g. the Ti–O bond length (1.824(5) Å) is considerably shorter in complex **1** than in complex **2** (2.05–2.06 Å). The value of the Ti–O-C angle (**1**; 152.9(5)°) indicates a pronounced sp-character of oxygen hybridization which favours  $\pi$ -bonding that reinforces the metal oxygen bond and consequently shortens the Ti–O bond length. This Ti–O bond strengthening renders formation of the active site (Cp<sub>2</sub>TiMe<sup>+</sup>) more difficult in compound **1** than that in compound **2** upon activation by MAO and supports the initial higher activity of **2** for ethylene polymerization (see below).

In contrast to **1** and **2**, no crystals could be obtained from **3** what precluded structural characterization by X-ray diffraction analysis. However, in the IR spectrum a band in the region of the NH stretch  $(3265 \text{ cm}^{-1})$  and the absence of band in the region of OH stretch points to coordination by the oxygen atom of the deprotonated

hydroxy group such as in complexes **1** and **2**. This proposal is reinforced by a signal in the <sup>1</sup>H NMR spectrum (5.25 ppm) attributable to NH whether no signal attributable to OH is visible. A downfield shift of the carbon atoms of the alkyne group (**3**; 95.8, 93.9, 90.5, and 87.0) in the <sup>13</sup>C NMR spectrum compared to the values in the free ligand (90.4, 89.4, 88.4, and 87.6) suggest the interaction of the alkyne group with titanium. A  $\eta^2$ -coordination (such as in **2**) involving the deprotonated hydroxyl group of the camphor ligand (<sup>3</sup>LH) and the adjacent alkyne group is feasible for **3**.

Coordination through the oxygen atoms of the sulphonyl group is excluded since no significant change in the stretching frequencies ( $v_{SO2 asym}$  1337,  $v_{SO2 asym}$  1149 cm<sup>-1</sup>) is observed upon coordination.

#### 2.2. Catalytic studies

The activity of complexes [TiClCp<sub>2</sub>L] (**1**, **2** and **3**), for ethylene polymerization was evaluated in toluene using MAO as co-catalyst. [TiCl<sub>2</sub>Cp<sub>2</sub>] was used as a standard catalyst for comparative purposes (Table 2, see experimental for conditions). To find the proper reaction conditions we screened the effect of the temperature and catalyst concentration using complex **1** (entries 1–4). We also checked the effect of increase of Al/Ti ratio on the polymerization activity (entry 4 versus 5).

Based on the initial set of experiments we decided to carry experiments with complexes **2** and **3** using conditions under which complex **1** displayed the highest polymerization activity (entry 4). The first conclusion is that compound **3** is no active for ethylene polymerization, conceivably due to its low solubility in toluene which is not improved by addition of MAO.

A look at the parameters that control the polymerization process indicates that catalysts **1** and **2** behave differently in what concerns the polymerization temperature. Catalyst **1** reaches maximum activity at 50 °C (Table 2, entry 4) while catalyst **2** is more efficient at RT (Table 2, entry 8). This behavior is based on the sp

| Table 2  |
|--|
| Data for polymerization of ethylene by $[TiClCp_2L]$ (1, 2). |

| Entry | Cat.                                 | <i>n</i> (Ti) [µmol] | <i>t</i> <sub>p</sub> [h] | T [°C] | Al/Ti | A <sup>a</sup> | $T_{m2}^{b} [^{\circ}C]$ | $\Delta H_{\rm m2}{}^{\rm b}$ (Jg <sup>-1</sup> ) | $M_{\rm n}^{\rm c}$ [kg mol <sup>-1</sup> ] | Ðc   |
|-------|--------------------------------------|----------------------|---------------------------|--------|-------|----------------|--------------------------|---|---|------|
| 1     | 1                                    | 3                    | 1                         | 22     | 1000  | 217            | 138                      | 190   |   |      |
| 2     | 1                                    | 1                    | 1                         | 22     | 1000  | 379            | 139                      | 123   |   |      |
| 3     | 1                                    | 1                    | 1                         | 80     | 1000  | 174            | 135                      | 198   |   |      |
| 4     | 1                                    | 1                    | 1                         | 50     | 1000  | 787            | 141                      | 165   |   |      |
| 5     | 1                                    | 1                    | 1                         | 50     | 2000  | 388            | 140                      | 173   |   |      |
| 6     | 1                                    | 1                    | 0.5                       | 50     | 1000  | 668            | 141                      | 173   | 91.9  | 2.70 |
| 7     | 2                                    | 1                    | 1                         | 50     | 1000  | 503            | 142                      | 181   |   |      |
| 8     | 2                                    | 1                    | 1                         | 22     | 1000  | 761            | 137                      | 137   |   |      |
| 9     | 2                                    | 1                    | 0.5                       | 50     | 1000  | 852            | 142                      | 180   | 89.2  | 2.67 |
| 10    | [TiCl <sub>2</sub> Cp <sub>2</sub> ] | 1                    | 0.5                       | 50     | 1000  | 670            | 141                      | 186   | 54.9  | 2.70 |

Experimental:  $p(C_2H_4) = 110$  kPa, toluene 40 mL, activated by MAO.

<sup>a</sup> Polymerization activity in kg<sub>PE</sub>mol<sup>-1</sup>h<sup>-1</sup>.

<sup>b</sup> Melting temperature and enthalpy determined by DSC from 2nd heating run.

<sup>c</sup> Molar mass and dispersity (Đ) determined by SEC in 1,2,4-trichlorbenzene at 160 °C against PS standards with universal calibration.



Fig. 2. HT–SEC chromatograms of polyethylenes produced by catalysts [TiClCp<sub>2</sub>L] (1 and 2) and [TiCl<sub>2</sub>Cp<sub>2</sub>] activated by MAO at 50  $^{\circ}$ C.

character of the Ti–O bond that renders more difficult bond breaking and formation of the active site in **1**.

Since the polymerization activity is very high (at  $2.5 \ 10^{-5}$  M catalyst) mass transfer problems may occur, to avoid that we decreased the reaction time by one half on the final set of experiments (entries 6, 9 and 10). The results indicate that depending on the experimental conditions the catalytic activities displayed by compounds 1 and 2 are similar (compound 1, entry 6) or may be higher (compound 2, entry 9) than that of [TiCl<sub>2</sub>Cp<sub>2</sub>] (entry 10). Data in Table 2 also shows that although, at the first stage of the process, catalyst 2 is more active (easier to activate by MAO) than catalyst 1 (compare entries 6 and 9) it deactivates faster than catalyst 1 that remains active for longer periods (compare entries 4 and 7). The best activity was achieved using catalysts 2 at 50 °C under Al/Ti equal to 1000 and conducting the process for ½ hour (entry 9).

The polyethylenes obtained from reaction with **1** and **2** display molar masses within a narrow monomodal distribution which is

typical of single-site catalysts. Furthermore the distributions obtained from reaction with **1**, **2** or  $[TiCl_2Cp_2]$  are identical (Fig. 2) pointing to the same active site  $(Cp_2TiMe^+)$  being generated upon treatment with excess of MAO. The higher average molar mass of polyethylenes obtained by reactions with **1** and **2** compared to  $[TiCl_2Cp_2]$  is attributed more growing centres being available due to a more difficult replacement of the camphor ligand (**1** and **2**) compared to chloride ligand in  $[TiCl_2Cp_2]$ .

Despite the different polymerization activities the polyethylene's molar masses obtained by reaction with  $\mathbf{1}$  and  $\mathbf{2}$  are very similar suggesting the same residence time of the chain on the catalyst site which is very short compared to the overall period of the experiment. Within this period (30 min) the catalyst  $\mathbf{1}$  is still increasing activity while catalyst  $\mathbf{2}$  already starts to deactivate.

The microstructures of the polyethylenes were checked by NMR and by measurement of the melting points using DSC technique. The <sup>1</sup>H NMR spectra of all samples display just signals attributed to the backbone methylenes of the polyethylenes in agreement with a highly linear polymer with crystallinity (40–65%) depending on the catalyst and reaction conditions used. A tentative extension of the catalytic activity of compounds **1** and **2** to the polymerization of hex-1-ene show they are not active. However, compounds **1** and **2** efficiently catalyze the co-polymerization of ethylene with norbornene (Table 3).

The rate of ethylene/norbornene co-polymerization is slower than that of the homo-polymerization process but still stays at high values. Slow down of the process was expected due to the higher steric demands of norbornene (NB) that render interaction with the metal site more difficult or decrease of the polymerization activity could be due to nonbonding interactions between coordinated norbornene and norbornene unit at the end of the growing chain as observed before [9,10]. Increase of Al/Ti ratio does not lead to change of polymerization activity (Table 3, Entry 1 and 2).

SEC–MALLS analysis for determination of copolymers absolute molar masses could be performed at RT due to low Tg and little or no crystallinity of the copolymers.

Table 3

Copolymerization of ethylene with norbornene catalyzed by complexes [TiClCp<sub>2</sub>L] (1 and 2) activated by MAO in toluene at 50 °C.

|       |      | -     |                |                        |                                       |                               | -                                       |   |                        |
|-------|------|-------|----------------|------------------------|---------------------------------------|-------------------------------|---|---|------------------------|
| Entry | Cat. | Al/Ti | A <sup>a</sup> | $dn/dc^{b} [mLg^{-1}]$ | $M_n^{\rm b}$ [kg mol <sup>-1</sup> ] | $\bar{\mathrm{D}}^\mathrm{b}$ | $T_{\rm g}{}^{\rm c} [^{\circ}{\rm C}]$ | $T_{\rm m}{}^{\rm c} [^{\circ}{\rm C}]$ | NB <sup>d</sup> [mol%] |
| 1     | 1    | 1000  | 194            | 0.089                  | 74.5                                  | 1.49                          | 9                                       | -                                       | 14                     |
| 2     | 1    | 500   | 192            | 0.099                  | 67.8                                  | 1.56                          | 13                                      | -                                       | nd                     |
| 3     | 2    | 500   | 399            | 0.089                  | 52.5                                  | 1.92                          | 13                                      | 182                                     | 13                     |
|       |      |       |                |                        |                                       |                               |   |   |                        |

 $p(C_2H_4) = 110 \text{ kPa}$ , [NB] = 1.0 M, 1 h, 3 µmol Ti, total volume 10 mL, activated by MAO.

<sup>a</sup> Polymerization activity in kg<sub>P</sub>mol<sub>Ti</sub><sup>-1</sup>h<sup>-1</sup>.

<sup>b</sup> Refractive index increment, absolute molar mass and dispersity (Đ) determined by SEC-MALLS in CHCl<sub>3</sub> at 35 °C.

<sup>c</sup> Determined by DSC from 1st heating run.

<sup>d</sup> NB content in copolymer as determined by  $^{13}$ C NMR in C<sub>6</sub>D<sub>6</sub>/1,2,4-trichlorobenzene (10/90 v/v) at 80 °C.



**Fig. 3.** SEC chromatograms of NB/ethylene copolymers measured in CHCl<sub>3</sub> at 35 °C: trace 1 (Table 3, entry 1), trace 2 (Table 3, entry 2) and trace 3 (Table 3, entry 3).

Just in one case (Table 3, entry 3) the co-polymer was crystalline, thus melting and fast cooling was repeated to eliminate the crystallinity and facilitate solubility (*vide infra* for thermal properties of polymers). The SEC traces show a monomodal distribution (Fig. 3) confirming the true co-polymer character of the samples. The distribution of the molar mass in co-polymers is narrower than in the polyethylenes as a consequence of the high solubility of the growing polymer in polymerization media and the homogeneous (solution) character of polymerization process throughout its course. Close values of co-polymers refractive index increment (necessary for evaluation of light-scattering data) confirm a similar content of NB units in all samples.

Quantitative <sup>13</sup>C NMR spectroscopy (Fig. 4) was used to characterize the microstructure of copolymers [11,12] and determine the content of NB units according to Eq. (1)



**Fig. 5.** DSC traces of ethylene/norbornene copolymers prepared by **2**/MAO. (a) 1st heating run, (b) 2nd heating run and (c) **1**/MAO (2nd heating run) in toluene at 50 °C.

$$NB = \frac{200 \cdot I_{C7}}{I(C_{5,6+\alpha,\beta,\gamma,\delta})} [mol\%]$$
(1)

The NB contents of the co-polymers obtained from reactions with catalysts **1** and **2** are analogous, as expected for identical catalytic centers. The NMR spectra resemble those of the vinyl-type co-polymers with an analogous content of NB units obtained from catalysis with zirconocene [11]. The minor resonances in the regions of  $C_{2,3}$  and  $C_{1,4}$  (Fig. 4) are caused by NENEN (47.85 and 41.96 ppm) and EENEE (47.15 and 41.54 ppm) pentades suggesting isolated or alternating norbornene units in copolymer structure with no norbornene blocks.



Fig. 4. 500 MHz INVGATE <sup>13</sup>C NMR spectra of NB/ethylene copolymer obtined by 1/MAO at 50 °C, measured at 30 °C in CDCl<sub>3</sub>.

The thermal behavior of the copolymers was investigated by DSC showing that the glass transition temperatures occur close to 10 °C (Fig. 5) in agreement with less than 20 mol% of NB monomer units [7,13]. In the case of the co-polymer obtained using 2/ MAO the melting temperature was observed in first heating run. However, the melting endotherm disappeared in the second heating cycle by using a cooling rate (10 °C min<sup>-1</sup>) sufficiently fast to protect the rearrangement of copolymer chains back to crystalline domains. Repeated measurements made on the re-melted sample (that was stored for one day at RT) showed the formation of more regular crystalline domains (melting point 203 °C) in agreement with alternating NB/ethylene co-polymers [12,14].

#### 3. Conclusions

The new complexes [TiClCp<sub>2</sub>L] (1, 2) display *pseudo*-octahedral geometries. The camphor ligands bind to titanium through the oxygen atom of the hydroxo (1) or oxime (2) groups. In 2, a cooperative effect of the nitrogen atom of the oxime gives to the camphor ligand a bidentate character ( $\eta^2$ ). In 1 the Ti–O bond is short (1.824(5)) compared to that in 2 (2.06<sub>av</sub>) due to a pronounced sp-hybridization of the oxygen atom that favours  $\pi$ -donation and strengths the Ti–O bond.

Complexes **1** and **2** catalyze ethylene polymerization to high linear polymers with molecular weights in the range of 90 kg mol<sup>-1</sup>. At 50 °C the activity of complex **1** (668 kg<sub>PE</sub>mol<sup>-1</sup>h<sup>-1</sup>) is similar to that of [TiCl<sub>2</sub>Cp<sub>2</sub>L] (670 kg<sub>PE</sub>mol<sup>-1</sup>h<sup>-1</sup>) while that of **2** (852 kg<sub>PE</sub>mol<sup>-1</sup>h<sup>-1</sup>) is considerably higher. However, the biggest differences in the catalytic activities of **1** (379 kg<sub>PE</sub>mol<sup>-1</sup>h<sup>-1</sup>) and **2** (761 kg<sub>PE</sub>mol<sup>-1</sup>h<sup>-1</sup>) occur at RT. The relative lower activity of **1** is attributed to the more difficult generation of the active site by rupture of the Ti–O bond as consequence of the strengthening of the Ti–O bond. Increasing the temperature the effect looses relevance and the catalytic activities approach.

The activities of complexes **1** and **2** for ethylene with norbornene co-polymerization are lower than those for ethylene polymerization due to steric reasons. Besides, the activities follow the same trend as for ethylene polymerization, i.e. complex **1** ( $192 \text{ kg}_{\text{P}} \text{mol}_{\text{Ti}}^{-1} \text{h}^{-1}$ ) is less active than complex **2** ( $399 \text{ kg}_{\text{P}} \text{mol}_{\text{Ti}}^{-1} \text{h}^{-1}$ ).

The products of polymerization were characterized by NMR and DSC. Polyethylenes are highly linear with crystallinities between 40% and 65%. Polyethylene/norbornene co-polymers are of the vinyl-type with calculated NB content (13–14%) well in the expected range for species with low glass transition temperatures (13 °C). The absolute molar masses of the co-polymers display a narrow monomodal distribution that does not differ much from catalysts **1** to **2**.

#### 4. Experimental

All complexes were prepared and catalytic studies were performed under dinitrogen atmosphere using vacuum and Schlenk techniques.

Solvents were purchased from Sigma–Aldrich purified by conventional techniques and distilled before use. Triethylamine was purchased from *Acros-Organics* and dried over sodium wire. [TiCl<sub>2</sub>Cp<sub>2</sub>] was purchased from Sigma–Aldrich. Camphor derived compounds were prepared by published techniques [15,16].

Ethylene (Linde, 99.8%) was purified by passing through copper and molecular sieves columns to remove the traces of oxygen and water. Toluene was refluxed over sodium for several hours and freshly distilled before the polymerization. The content of water remaining in toluene was bellow 1 ppm as checked by repeated Karl–Fischer titration. MAO (Aldrich, 10% in toluene) was used as received. Norbornene was diluted in dry toluene and left standing over 4 Å molecular sieves several days to dry. IR spectra were obtained in a JASCO FT/IR 4100 spectrometer. NMR spectra of complexes (<sup>1</sup>H, <sup>13</sup>C, DEPT, HSQC HMBC) were obtained in CDCl<sub>3</sub> using Bruker Avance II<sup>+</sup> Spectrometers (300 or 400 MHz). TMS ( $\delta = 0$  ppm) was used as internal reference. <sup>1</sup>H NMR spectra of polyethylenes were obtained in 1,2,4-trichlorobenzene/C<sub>6</sub>D<sub>6</sub> (90/10 vol%) at 120 °C using a 500 MHz Bruker Avance DRX 500 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra of ethylene/NB copolymers were obtained in CDCl<sub>3</sub> at 30 °C or in 1,2,4-trichlorobenzene/C<sub>6</sub>D<sub>6</sub> (90/10 v/v) at 80 °C. Concentration of samples was 20–30 mg/mL. Quantitative INVGATE <sup>13</sup>C NMR spectra were acquired with  $d_1 = 10$  s, 90° pulse and at least 2000 scans. NMR signals were assigned according to literature [11,12].

Melting temperatures and melting enthalpies of polyethylenes were measured by DSC using a TA Instruments, Q100 and evaluated from the second heating run using heating and cooling rate  $10 \,^{\circ}\text{Cmin}^{-1}$ . Crystallinity of polyethylenes was calculated using the melting enthalpy value 297 J/g for 100% crystalline polyethylene.

Polyethylene's molar masses and dispersities were determined by SEC in 1,2,4-trichlorobenzene (TCB) at 160 °C using PL-GPC 220 chromatograph equipped with differential refractometer and viscometric detector on PS standards and universal calibration method. Separation was performed on three PL gel 10  $\mu$ m MIXED-B (300  $\times$  7.5 mm)column set at TCB flow rate 1 mL/min. Samples solutions in TCB (1 mg/mL) were stabilized by 0.025 wt% of Santanox R.

#### 4.1. Synthesis of complexes

4.1.1. Complexes [TiClCp<sub>2</sub>L] were typically prepared in triethylamine upon exposition to sun-light as described for complex **1** 

 $[TiClCp_2(^1L)]$  (1) – A suspension of  $[TiCl_2Cp_2]$  (106 mg, 0.425 mmol),  $C_{10}H_{17}NSO_3$  (100 mg, 0.432 mmol) and triethylamine (10 mL) was exposed to sun-light and stirred for 2 h affording a yellow suspension that was filtered off solution and dried under vacuum to remove triethylamine. The yellow compound was then dissolved in fresh distilled toluene (50 mL) and filtered to remove by-products. The solvent was then reduced to ca. half volume and the solution was left in the fridge  $(-20 \circ C)$  overnight. Orange-yellow crystals formed that were filtered off solution and dried (100 mg, Yield 60%). Elemental analysis for [TiClCp<sub>2</sub>(C<sub>10</sub>H<sub>16</sub>NSO<sub>3</sub>)]·6/7 C<sub>7</sub>H<sub>8</sub>. Anal. Calc.: C, 59.8; N, 2.9; H, 6.2; S, 6.1. Found: C, 59.2; N, 2.3; H, 6.1; S, 5.7%. IR (cm<sup>-1</sup>): 3228 (*v*<sub>NH</sub>); 3094 (Cp<sub>ring</sub>); 1130, 1108 (*v*<sub>SO2</sub>); 815 (Cp<sub>ring</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm): 6.31 (s, 5H), 6.34 6.31 (s, 5H), 4.82 (d, *J*<sub>HH</sub> = 7.2, 1H), 3.55 (d, *J*<sub>HH</sub> = 7.2, 1H), 3.52(d, *J*<sub>HH</sub> = 7.2, 1H), 3.10 (s, 2H), 1.91 (s<sub>br</sub>, 1H), 1.87–1.72 (m, 2H), 1.35–1.22 (m, 2H), 1.19 (s, 3H), 0.85 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 117.1, 117.0, 93.9, 69.7, 56.5, 50.9, 50.6, 47.4, 30.4, 23.9, 22.0, 21.0.

[TiClCp<sub>2</sub>(<sup>2</sup>L)] (**2**) – [TiCl<sub>2</sub>Cp<sub>2</sub>] (68 mg, 0.273 mmol) *plus*  $C_{10}H_{16}NO_2$  (50 mg, 0.276 mmol) were stirred for 2 h. Upon work up yellow crystals of **2** were obtained (120 g, Yield 54%). Elemental analysis for [TiClCp<sub>2</sub>( $C_{10}H_{15}NO_2$ )] *Anal.* Calc.: C, 61.0; N, 3.6; H, 6.1. Found: C, 61.3; N, 3.9; H, 6.6%. IR (cm<sup>-1</sup>): 3098 (Cp<sub>ring</sub>); 1733 ( $\nu_{CO}$ ); 1609 ( $\nu_{CN}$ ); 811 (Cp<sub>ring</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 6.05 (s, 5H), 6.01 (s, 5H), 3.29 (d, *J*<sub>HH</sub> = 4.4, 1H), 2.14–2.06 (m, 1H), 1.91–1.83 (m, 1H), 1.63–1.57 (m, 1H), 1.52–1.46 (m, 1H), 1.10 (s, 3H), 1.02 (s, 3H), 0.94 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 203.2, 151.6, 115.2, 115.1, 59.2, 49.9, 46.3, 30.9, 24.2, 20.9, 17.9, 9.0.

[TiClCp<sub>2</sub>(<sup>3</sup>LH)] (**3**) – [TiCl<sub>2</sub>Cp<sub>2</sub>] (58 mg, 0.23 mmol) *plus*  $(C_{26}H_{25}NSO_3, {}^{3}LH_2)$  (100 mg, 0.23 mmol) were stirred for 1 h. The solvent was evaporated to dryness and the solid washed with MeOH (20 mL). Then, the orange powder was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and allowed to precipitate in the fridge. Upon filtration and drying under vacuum compound **3** was obtained. (110 mg, Yield 74%). Elemental analysis for [TiClCp<sub>2</sub>(C<sub>26</sub>H<sub>24</sub>NSO<sub>3</sub>)]  $\frac{1}{2}$ CH<sub>2</sub>Cl<sub>2</sub>. *Anal.* Calc.: C, 63.9; N, 2.0; H, 5.1; S, 4.7. Found: C, 63.5; N, 2.3; H, 5.1; S, 4.9%. IR (cm<sup>-1</sup>): 3055 (Cp<sub>ring</sub>); 3265 ( $\nu_{NH}$ ); 2227 ( $\nu_{CC}$ ); 817

#### Table 4

Crystallographic data for complexes [TiClCp\_2L\_1] (1) and [TiClCp\_2L\_2] (2) obtained at 150 K.

|                                 | $[TiClCp_2L_1]$ (1)                                   | [TiClCp <sub>2</sub> L <sub>2</sub> ]<br>( <b>2</b> ) |
|---------------------------------|---|---|
| Empirical formula               | C <sub>27</sub> H <sub>34</sub> NO <sub>3</sub> CISTi | C40H48N2O4Cl2Ti2                                      |
| Formula weight                  | 535.96  | 812.6   |
| Temperature (K)                 | 150   | 150   |
| Wavelength                      | 0.71073   | 0.71073   |
| Crystal system                  | orthorhombic  | orthorhombic  |
| Space group                     | $P2_{1}2_{1}2_{1}$                                    | $P2_{1}2_{1}2_{1}$                                    |
| Unit cell dimensions            |   |   |
| a (Å)                           | 9.9815(4)   | 12.775(1)   |
| b (Å)                           | 13.8014(6)  | 13.607(1)   |
| c (Å)                           | 18.552(1)   | 21.586(2)   |
| α (°)                           | 90  | 90  |
| β (°)                           | 90  | 90  |
| γ (°)                           | 90  | 90  |
| Volume (A <sup>-3</sup> )       | 2555.6(2)   | 3752.3(5)   |
| Ζ                               | 4   | 4   |
| $D_{cal}$ (g/cm <sup>3</sup> )  | 1.393   | 1.394   |
| Absorption                      | 0.551   | 0.611   |
| coefficient                     |   |   |
| $(mm^{-1})$                     |   |   |
| F(000)                          | 1128  | 1648  |
| Crystal size (mm <sup>3</sup> ) | $0.2\times0.3\times0.2$                               | $0.3\times0.3\times0.2$                               |
| $\theta$ range for data         | 1.84-21.02  | 1.77-30.86  |
| collection (°)                  |   |   |
| Index ranges                    | $-10 \leqslant h \leqslant 9$ ,                       | $-18 \leqslant h \leqslant 16$ ,                      |
|                                 | $-12\leqslant k\leqslant 13$ ,                        | $-16\leqslant k\leqslant 19$ ,                        |
|                                 | $-14 \leqslant l \leqslant 18$                        | $-31\leqslant l\leqslant 24$                          |
| Refinement                      | Full-matrix least-squares                             | Full-matrix least-squares                             |
| method                          | on F <sup>2</sup>                                     | on $F^2$  |
| Data/restraints/                | 2558/0/295  | 11468/0/451   |
| parameters                      |   |   |
| Final R (observed)              | $R_1 = 0.049, wR_2 = 0.125$                           | $R_1 = 0.033, wR_2 = 0.083$                           |

(TiCp<sub>ring</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$  ppm): 7.4–7.2 (m, 10H), 6.50 (s, 5H), 6.38 (s, 5H), 5.25 (s, 1H), 3.27, 3.21 (2d, *J*<sub>HH</sub> = 13.7, 2H), 2.31–1.75 (m, 5H), 1.26 (s, 3H), 1.01 (s, 3H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$  ppm): 132.29, 132.25, 132.23, 132.11, 129.31, 129.17, 129.09, 128.91, 128.85, 128.80, 123.2, 122.9, 119.8, 118.8, 95.8, 93.9, 90.5, 87.0, 64.7, 57.8, 51.9, 46.3, 28.6, 24.6, 24.3, 23.4.

#### 4.2. Catalytic studies

The general procedure used in the catalytic studies was: first the toluene (polymerization) or norbornene solution in toluene (co-polymerization) was cannula transferred to the reactor, followed by addition of MAO solution against the flow of ethylene and thermostated to polymerization temperature. Polymerization was started by injection of the catalyst solution that had been prepared in toluene by weighing at least of 20 mg of catalyst and kept in fridge at 5 °C. Homo- and co-polymerization processes were performed in double-walled magnetically stirred glass reactor at 110 kPa ethylene pressure. After the desired polymerization time the reaction was quenched by addition of EtOH/HCl mixture, polymer was precipitated to large excess of acidified EtOH, filtered, washed and dried in vacuum oven at 50 °C overnight.

#### 4.3. X-ray diffraction analysis

X-ray diffraction analysis was performed on red crystals of  $[TiClCp_2L]$  (L = <sup>1</sup>L, (1); <sup>2</sup>L, (2)). Data was collected on a Bruker

AXS-KAPPA APEX II area detector apparatus using graphitemonochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) and were corrected for Lorentz, polarization and empirically for absorption effects. Cell dimensions were determined from the setting angles of reflections (26552 for 1) and 6227 for 2). Complexes 1 and 2 crystallize in the orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. The structures were solved by direct methods using SHELX97 [17] and refined by full matrix least squares against *F*<sup>2</sup> using SHELX97 all included in the suit of programs WinGX v1.70.01 for Windows [18]. Non-hydrogen atoms were refined anisotropically and H atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atom. A molecule of toluene was found to co-crystallize with 1 and refined. In the structure of 2 exist two independent molecules *per* asymmetric unit that were refined.

Crystal data and refinement parameters are summarized in Table 4. Illustrations of the molecular structures were made with ORTEP3 [19].

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#### Appendix A. Supplementary material

CCDC 846830 & 846831 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.11.019.

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#### Fluorosilyl-Substituted Cyclopentadienyltitanium(IV) Complexes: Synthesis, Structure, and Styrene Polymerization Behavior<sup>#</sup>

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The synthesis and characterization of new halo-silyl-substituted titanium(IV) derivatives  $[TiCl_3(\eta^5 - \tau)]$  $C_5H_4SiCl_3$ ] (9), [TiCl\_3( $\eta^5$ - $C_5H_4SiMe_2F$ )] (10), [TiCl\_3( $\eta^5$ - $C_5H_4SiMe_F_2$ )] (11), [TiCl\_3( $\eta^5$ - $C_5H_4SiF_3$ )] (12), and  $[TiF_3(\eta^5-C_5H_4SiMe_2F)]$  (13) are reported. The reaction of lithiated trimethylsilylcyclopentadienide with Me<sub>2</sub>SiCl<sub>2</sub>, MeSiCl<sub>3</sub>, or SiCl<sub>4</sub> gave chlorosilyl(trimethylsilyl)cyclopentadienes that were fluorinated with Me<sub>3</sub>SnF to yield fluorosilyl derivatives  $C_5H_4$ (SiMe<sub>2</sub>F)SiMe<sub>3</sub> (4),  $C_5H_4$ (SiMeF<sub>2</sub>)SiMe<sub>3</sub> (5), and  $C_5H_4$ - $(SiF_3)SiMe_3$  (6), respectively. Addition of disilylated compounds 4-6 to a solution of TiCl<sub>4</sub> gave the respective half-sandwich titanium complexes 10-12, which could be alternatively prepared by selective fluorination of the corresponding chlorosilyl-substituted cyclopentadienyltitanium(IV) trichlorides with Me<sub>3</sub>SnF. Completely fluorinated  $[TiF_3(C_5H_4SiMe_2F)]$  (13) was prepared from  $[TiCl_3(C_5H_4SiMe_2Cl)]$  (7) and 4 equiv of Me<sub>3</sub>SnF. The molecular structures of the pentameric 13 and the monomeric 10 were determined by X-ray diffraction analysis. The 47,49Ti NMR and UV-vis spectroscopy showed the electronreleasing nature of the SiMe<sub>2</sub>Cl, SiMe<sub>2</sub>F, SiMeCl<sub>2</sub>, and SiMeF<sub>2</sub> substituents, whereas SiCl<sub>3</sub> and SiF<sub>3</sub> groups had electron-withdrawing properties. The catalytic behavior of these half-sandwich titanium compounds in styrene polymerization was studied in the presence of excess methylaluminoxane.

#### Introduction

Group 4 metallocenes represent an important class of organometallic compounds that are applicable as catalysts in homogeneous polymerization<sup>1</sup> of olefins. The substitution on the cyclopentadienyl ring is the main route used for modifying the properties of these complexes.<sup>2</sup> Whereas the initial step of the catalytic process is the attack of the electron-rich olefin on the electron-deficient metal center,<sup>3</sup> one can anticipate that decreasing the electron density at the central metal atom will lead to an increased polymerization activity of the modified catalyst. In 1986, Gassman and Winter reported preparation and characterization of the first titanocene complex bearing a strongly electron-withdrawing CF<sub>3</sub> substituent.<sup>4</sup> Since that time the syntheses of Group 4 compounds with electron-withdrawing chloro,<sup>5</sup> carbomethoxy,<sup>6</sup> carboxamide,<sup>7</sup> or perfluoroaryl<sup>8</sup> sub-

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stituents on the cyclopentadienyl ring have been published, and some of these complexes were used as olefin polymerization catalysts.9 Recently, the synthesis<sup>10-12</sup> and reactivity studies<sup>13,14</sup> of chlorosilyl-substituted cyclopentadienyltitanium(IV) compounds were published, but their electronic properties were not investigated.

We report here the syntheses of novel titanium complexes bearing trichlorosilyl-, fluoro(dimethyl)silyl-, difluoro(methyl)silyl-, and trifluorosilyl-substituted cyclopentadienyl ligands. All compounds were characterized by spectroscopic methods in order to determine electronic effects of the halosilyl substituents on the titanium atom. We also present results of our studies of styrene polymerization catalyzed by these complexes in the presence of an excess of methylaluminoxane.

#### **Results and Discussion**

Synthesis and Characterization of Ligands. 1-(Trichlorosilyl)-1-(trimethylsilyl)cyclopentadiene (3) was prepared by

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<sup>#</sup> Dedicated to Dr. Karel Mach on the occasion of his 70th birthday. \* To whom all correspondence should be addressed. E-mail:

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the reaction of (trimethylsilyl)cyclopentadienyllithium with silicon tetrachloride in hexane according to the methods described for the chloro(dimethyl)silyl<sup>10</sup> and dichloro(methyl)-silyl<sup>11</sup> derivatives **1** and **2**, respectively; see Scheme 1.

Scheme 1 depicts the reactions of the silyl-disubstituted cyclopentadienes 1-3 with a common fluorinating agent, Me<sub>3</sub>-SnF,<sup>23</sup> to give the respective fluorosilyl derivatives C<sub>5</sub>H<sub>4</sub>-(SiMe<sub>2</sub>F)SiMe<sub>3</sub> (4), C<sub>5</sub>H<sub>4</sub>(SiMeF<sub>2</sub>)SiMe<sub>3</sub> (5), and C<sub>5</sub>H<sub>4</sub>(SiF<sub>3</sub>)-SiMe<sub>3</sub> (6). <sup>1</sup>H and <sup>19</sup>F NMR spectroscopic studies showed that the irreversible replacement of chlorine atom(s) by fluorine is complete in 30 min at ambient temperature.

<sup>19</sup>F NMR spectroscopy showed that the reaction of **3** with Me<sub>3</sub>SnF proceeded rapidly and completely at ambient temperature giving 1-(trifluorosilyl)-1-(trimethylsilyl)cyclopentadiene (**6**). However, purification of **6** by vacuum distillation was only partially successful since large amounts of the Me<sub>3</sub>SnCl produced in the reaction always contaminated the product. Hence we used Bu<sub>3</sub>SnF instead of Me<sub>3</sub>SnF. Thus, after vacuum distillation, analytically pure product could be isolated.

**Preparation of Titanium(IV) Complexes.** Treatment of  $C_5H_4(SiCl_3)SiMe_3$  (3) with TiCl<sub>4</sub> in dichloromethane or toluene gave [TiCl<sub>3</sub>( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiCl<sub>3</sub>)] (9) with selective elimination of Me<sub>3</sub>SiCl (Scheme 2). The yellow product 9 is moderately soluble in organic solvents and was easily purified by crystallization from hexane or vacuum sublimation. Titanium complex 9 is air- and moisture-sensitive but could be stored as a solid under inert atmosphere. Toluene or dichloromethane solutions of 9 slowly turned green-yellow on standing in direct light under argon at ambient temperature. Similar behavior of related half-metallocenes [TiCl<sub>3</sub>( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>Cl)] (7) and [TiCl<sub>3</sub>( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-SiMeCl<sub>2</sub>)] (8) was described by Royo et al.<sup>11</sup>

The fluorosilyl-substituted cyclopentadienes 4-6 reacted with titanium tetrachloride to give new half-sandwich titanium(IV)

trichlorides 10-12 bearing fluorosilyl substituents on the Cp ring. Compounds 10-12 are moisture-sensitive bright yellow microcrystalline solids that can be purified by crystallization from hexane or, better, by vacuum sublimation. The multinuclear NMR spectra were consistent with their proposed structures. For details see the Experimental Section.

An alternative method for the preparation of complexes 10-12 is the selective fluorination of the corresponding chlorosilylsubstituted metallocenes 7-9 by Me<sub>3</sub>SnF (Scheme 3). NMR spectroscopy showed that fluorination is very selective, and Ti-Cl bonds remain untouched when the molar amount of Me<sub>3</sub>-SnF used is less than or equal to the number of Si-Cl bonds. Selectivity of the fluorination process was also confirmed by the determination of the molecular structure of 10.

If an excess of the fluorination agent is used, fluorides readily replace all chlorine atoms in the molecule. We isolated and characterized the compound  $[TiF_3(\eta^5-C_5H_4SiMe_2F)]$  (13) and determined its molecular structure. The oligomeric nature of 13 in a solution was evidenced by very broad signals in the <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra. A broad <sup>19</sup>F resonance at 173.42 ppm corresponds to fluorine nuclei bonded to the titanium atom. All attempts to prepare fluorosilyl-cyclopentadienyl titanium-(IV) trifluorides of the formula  $[TiF_3(\eta^5-C_5H_4SiMeF_2)]$  (14) and  $[TiF_3(\eta^5-C_5H_4SiF_3)]$  (15) led to completely insoluble orange solids that could not be satisfactorily characterized.

<sup>47,49</sup>Ti NMR and Electronic Absorption Spectra. It was demonstrated previously<sup>16,17</sup> that the introduction of electronreleasing groups (alkyl, trimethylsilyl, trimethylstannyl, etc.) on the cyclopentadienyl ring leads to a decrease of the HOMO– LUMO energy gap and results in an increase of  $\lambda_{max}$  (wavelength of the first CT band in the electronic spectra) as well as in a downfield shift of the  $\delta$ (Ti) signal in the <sup>47,49</sup>Ti NMR spectrum. We used Ti NMR and UV–vis spectroscopy to assess the electronic effects of halosilyl substituents on the metal nucleus. Table 1 lists <sup>47,49</sup>Ti NMR data and  $\lambda_{max}$  values for the studied complexes together with corresponding data for related halfsandwich titanium(IV) trichlorides. We note that no interactions between <sup>47,49</sup>Ti and <sup>19</sup>F nuclei were observed in the NMR spectra of fluorosilyl complexes **10** and **11**.

When parent complex CpTiCl<sub>3</sub> is considered to be a reference, all substituted compounds with higher  $\lambda_{max}$  and  $\delta(Ti)$  values have greater electron density at the titanium atom; that is, the substituent on the cyclopentadienyl ring has an electron-donating effect. From obtained data it is evident that SiMe<sub>2</sub>Cl, SiMe<sub>2</sub>F, SiMeCl<sub>2</sub>, and SiMeF<sub>2</sub> groups show features typical for electronreleasing substituents. The introduction of the SiCl<sub>3</sub> group causes a high-field shift of  $\delta(Ti)$  by 4.1 ppm. Analogously, the electronwithdrawing properties of SiCl<sub>3</sub> and SiF<sub>3</sub> groups cause a blueshift of  $\lambda_{max}$  values by 4 and 19 nm, for complexes 9 and 12, respectively.

Chart 1 shows the dependence of  $\delta({}^{49}\text{Ti})$  and  $\lambda_{\text{max}}$  on the nature of the substituent bonded to the cyclopentadienyl ring; data for complex [TiCl<sub>3</sub>( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)] and reference compound CpTiCl<sub>3</sub> are included for the purpose of comparison. The properties of the substituent on the cyclopentadienyl ring change from electron-releasing to electron-withdrawing in the order

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Table 1. <sup>47,49</sup>Ti NMR Data and Absorption Maxima of the First CT Transition in Electronic Spectra

|   |                                | •  |                              |  | ·                     |           |
|---|--------------------------------|--|------------------------------|--|-----------------------|-----------|
| compound                                | $\delta(^{49}\text{Ti})$ [ppm] | $\Delta \nu_{1/2}$ <sup>(49</sup> Ti) [Hz] | $\delta(^{47}{ m Ti})$ [ppm] | $\Delta \nu_{1/2}$ <sup>(47</sup> Ti) [Hz] | $\lambda_{\max}$ [nm] | ref       |
| 7                                       | $-369.3^{a}$                   | 69   | -635.8                       | 172  | 398                   | 16        |
| 8                                       | $-387.0^{b}$                   | 97   | -652.7                       | 255  | 391                   | this work |
| 9                                       | $-402.3^{b}$                   | 211  | -668.8                       | 923  | 377                   | this work |
| 10                                      | $-372.1^{b}$                   | 81   | -639.5                       | 229  | 396                   | this work |
| 11                                      | $-394.1^{b}$                   | С  | d                            | d  | 382                   | this work |
| 12                                      | d                              | d  | d                            | d  | 362                   | this work |
| CpTiCl <sub>3</sub>                     | $-396.5^{e}$                   | 49   | -662.7                       | 74   | 381                   | 16        |
| (Me <sub>3</sub> SiCp)TiCl <sub>3</sub> | $-361.4^{a}$                   | 36   | -628.0                       | 85   | 400                   | 16        |
|   |                                |  |                              |  |                       |           |

<sup>a</sup> CD<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> Toluene-d<sub>8</sub>. <sup>c</sup> Not determined. <sup>d</sup> Too broad to be observed. <sup>e</sup> CDCl<sub>3</sub>.

Chart 1. Dependence of  $\lambda_{max}$  and  $\delta(^{49}\text{Ti})$  on the Nature of the Substituent R in the Series of RC<sub>5</sub>H<sub>4</sub>TiCl<sub>3</sub> Complexes<sup>a</sup>



a Dashed lines correspond to data for reference compound CpTiCl<sub>3</sub>.

Chart 2. Correlation between  $\delta(^{49}\text{Ti})$  and  $\lambda_{\text{max}}$  for the Complexes 7–11



 $SiMe_3 > SiMe_2Cl > SiMe_2F > SiMeCl_2 > SiMeF_2 \approx H > SiCl_3 > SiF_3.$ 

Similar to the other half-sandwich titanium(IV) trihalides, a nearby linear relationship (correlation coefficient = 0.9808) between the <sup>49</sup>Ti NMR chemical shift and  $\lambda_{max}$  was found; see Chart 2. The principles of this phenomenon were explained elsewhere in terms of variation in the paramagnetic contribution to the Ti nucleus shielding.<sup>17</sup> For the series of the presently studied compounds this implies a similar character of their frontier orbitals.

The next NMR parameter observed,  $^{47,49}$ Ti resonance halfwidth at half-height ( $\Delta v_{1/2}$ ), is usually attributed to the symmetry or asymmetry of the electronic environment at the titanium atom. Since the electronic environment at the titanium atom is affected



Figure 1. Thermal ellipsoid plot (50% probability) of 10. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ti1-Cg1, 2.001(1); Ti1-Cl1, 2.2320(9); Ti1-Cl2, 2.2230(9); Ti1-Cl3, 2.2336(9); Cl1-Ti1-Cl2, 104.76(4); Cl2-Ti1-Cl3, 101.89(4); Cl1-Ti1-Cl3, 102.98(4).

by substituents bonded to the cyclopentadienyl ring, it is not surprising that the changes in the number of halogen atoms bonded to the Si atom cause variation in  $\Delta \nu_{1/2}$ . In the series of studied complexes <sup>47,49</sup>Ti resonance half-widths increase with an increasing number of halide atoms on the silyl group and increase on going from a less electronegative chlorosilyl to a more electronegative fluorosilyl substituent. The largest  $\Delta \nu_{1/2}$ value was observed for trichlorosilyl complex 9, and significant line broadening prevented the Ti nucleus resonance signal for [TiCl<sub>3</sub>( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiF<sub>3</sub>)] (**12**) from being observed.

**Crystal Structure.** In the crystals of **10**, two crystallographically independent but essentially identical molecules are present. The structure of one of them is depicted in Figure 1, together with the atomic numbering scheme. Crystallographic data are listed in Table 4. In the molecule of **10** the cyclopentadienyl ring is almost planar, with no carbon atom deviating more than 0.01 Å. The coordination of the Ti atom can be described as a three-legged piano-stool configuration, with geometrical parameters very close to those reported for  $[TiCl_3(C_5H_4SnMe_3)]$ , or  $[TiCl_3(C_5H_4SnMe_2Ph)]$ .<sup>18</sup> The fluorine atom is located below the cyclopentadienyl ring plane. The Ti···F separation is 3.652(2) Å [3.575(2) Å] (hereafter, the values in brackets refer to the second independent molecule). The dihedral angle between the cyclopentadienyl ring plane and the C<sub>ipso</sub>-Si bond vector is 1.5(2)° [0.1(2)°].

There are two independent (13A and 13B) molecules with minor structural differences in the unit cell of 13. Table 2 lists selected geometric parameters for 13A that will be used in the subsequent discussion. Crystallographic data are summarized

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Table 2. Selected Geometric Parameters for 13 (species A)

|             |           | Bond Leng   | ths (Å)   |             |           |
|-------------|-----------|-------------|-----------|-------------|-----------|
| Ti1-Cg1     | 2.025(2)  | Ti1-F12     | 1.813(2)  | Ti2-F13     | 1.975(2)  |
| Ti2-Cg2     | 2.054(1)  | Ti1-F13     | 2.037(2)  | Ti2-F23     | 1.967(2)  |
| Ti3-Cg3     | 2.076(1)  | Ti1-F14     | 1.805(2)  | Ti2-F22     | 2.035(1)  |
| Ti4-Cg4     | 2.067(1)  | Ti1-F15     | 1.939(2)  | Ti1····Ti2  | 3.3100(7) |
| Ti5-Cg5     | 2.030(1)  | Ti2-F15     | 2.159(2)  | Ti3····Ti4  | 3.3039(6) |
|             |           | Bond Angle  | es (deg)  |             |           |
| F12-Ti1-F13 | 72.15(7)  | Cg2-Ti2-F15 | 172.54(6) | F16-Ti2-F22 | 151.35(7) |
| F12-Ti1-F14 | 80.48(8)  | Cg2-Ti2-F16 | 104.88(7) | Ti1-F15-Ti2 | 107.63(7) |
| F13-Ti1-F15 | 90.94(10) | F13-Ti2-F23 | 150.04(7) | Ti2-F23-Ti4 | 148.98(8) |

 Table 3. Results of Styrene Polymerization Catalyzed by

 Studied Compounds<sup>a)</sup>

| catalyst            | Al/Ti | conversion<br>[%] | A <sup>b</sup> | $M_n^c$<br>[kg•mol <sup>-1</sup> ] | $M_{\rm w}/M_{\rm n}^c$ | $T_{\rm m}^{d}$ [°C] |
|---------------------|-------|-------------------|----------------|------------------------------------|-------------------------|----------------------|
| CpTiCl <sub>3</sub> | 800   | 98                | 89             | 8.6                                | 2.47                    | 252.7                |
| 7                   | 800   | 99                | 89             | 16.1                               | 2.34                    | 266.1                |
| 8                   | 800   | 93                | 84             | е                                  | е                       | 264.6                |
| 9                   | 800   | 89                | 81             | е                                  | е                       | 265.1                |
| 10                  | 800   | 81                | 73             | 64.0                               | 2.32                    | 263.9                |
| 11                  | 800   | 99                | 89             | 57.4                               | 2.35                    | 264.3                |
| 12                  | 800   | 87                | 79             | е                                  | е                       | 265.1                |
| 13                  | 400   | 51                | 46             | 17.5                               | 2.24                    | 266.5                |
|                     | 800   | 47                | 42             |                                    |                         |                      |
|                     | 1600  | 53                | 18             |                                    |                         |                      |

<sup>*a*</sup> Polymerization conditions: [Ti] = 300  $\mu$ M, [styrene] = 0.52 M, reaction time 2 h, toluene, 50 °C, total volume 30 mL. <sup>*b*</sup> Activity: kg PS/ (mol<sub>Ti</sub><sup>-1</sup> × h<sup>-1</sup>). <sup>*c*</sup> Determined by SEC. <sup>*d*</sup> Melting temperature of polystyrene. <sup>*e*</sup> Not determined due to insolubility of polymer in 1,2,4-trichlorobenzene.

Table 4. Crystallographic Data for 10 and 13

|                                    | 10                             | 13                            |
|------------------------------------|--------------------------------|-------------------------------|
| empirical formula                  | C7H10Cl3FsiTi                  | C35H50F20Si5Ti5               |
| cryst syst                         | triclinic                      | monoclinic                    |
| space group                        | <i>P</i> 1 (No. 2)             | $P2_1/c$ (No. 14)             |
| <i>a</i> (Å)                       | 6.4370(3)                      | 14.0743(1)                    |
| b (Å)                              | 12.5910(5)                     | 26.4287(2)                    |
| <i>c</i> (Å)                       | 14.9830(10)                    | 26.6932(2)                    |
| α (deg)                            | 96.361(5)                      | 90                            |
| $\beta$ (deg)                      | 12.5910(5)                     | 93.2874(5)                    |
| $\gamma$ (deg)                     | 92.040(5)                      | 90                            |
| Ζ                                  | 4                              | 8                             |
| $V(Å^3)$                           | 1168.54(11)                    | 9912.61(13)                   |
| $D_{\rm c} ({\rm g}{\rm cm}^{-3})$ | 1.680                          | 1.649                         |
| cryst size (mm)                    | $0.3 \times 0.25 \times 0.075$ | $0.3 \times 0.25 \times 0.15$ |
| cryst shape                        | yellow plate                   | orange plate                  |
| $\mu (\mathrm{mm}^{-1})$           | 1.486                          | 0.994                         |
| F(000)                             | 592                            | 4960                          |
| h; k; l range                      | -8, 8; -16, 16;                | -18, 18; -34, 34;             |
|                                    | -19, 19                        | -34, 34                       |
| $\theta$ range (deg)               | 1.37-27.5                      | 1.45-27.5                     |
| no. of reflns measd                | 17 673                         | 149 981                       |
| no. of indep reflns                | 5358 (0.016)                   | 22 749 (0.056)                |
| $(R_{\rm int})^a$                  |                                |                               |
| no. of obsd reflns                 | 3284                           | 16 586                        |
| $[I \ge 2\sigma(I)]$               |                                |                               |
| no. of params refined              | 235                            | 1191                          |
| max./min. $\Delta \rho$            | 0.576/-0.733                   | 0.508/-0.432                  |
| $(e \dot{A}^{-3})$                 |                                |                               |
| $GOF^{b}$                          | 1.228                          | 1.076                         |
| $R^{c}/wR^{c}$                     | 0.035/0.0893                   | 0.0385/0.0929                 |
|                                    |                                |                               |

 ${}^{a} R_{\text{int}} = \sum |F_{o}^{2} - F_{o,\text{mean}}^{2}| / \sum F_{o}^{2} \cdot {}^{b} \text{ GOF} = [\sum (w(F_{o}^{2} - F_{c}^{2})^{2}) / (N_{\text{diffs}} - N_{\text{params}})]^{1/2} \text{ for all data.} {}^{c} R(F) = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}| \text{ for observed data,} wR(F^{2}) = [\sum (w(F_{o}^{2} - F_{c}^{2})^{2}) / (\sum w(F_{o}^{2})^{2})]^{1/2} \text{ for all data.}$ 

in Table 4. The molecular structure of **13** in the solid state consists of a pentameric unit (Figure 2) in which three titanium atoms are coordinated in a distorted octahedral fashion, whereas the remaining two titanium atoms, Ti1 and Ti5, have a coordination environment near that of a tetragonal pyramid. The  $Ti_4F_{12}$  core has geometric parameters similar to those reported

for the tetrameric compound  $[TiF_3(\eta^5-C_5Me_4Et)]_4$ .<sup>19</sup> The fifth molecule in 13 is connected to this core through two bridging fluorine atoms, F13 and F15. The terminal (mean 1.822 Å) and bridging Ti-F bond lengths (mean 2.010 Å) show the expected differences. The complete structure involving substituted cyclopentadienyl rings is depicted in Figure 3. Silicon-bonded fluorine atoms do not participate in the formation of bridges. The metal-ring distances at titanium atoms Ti1 and Ti5 are slightly shorter than those found for the hexacoordinated metal centers Ti2, Ti3, and Ti4. Silicon-bonded fluorine atoms F11, F21, F41, and F51 are located above their parent cyclopentadienyl ring planes, away from the titanium center. Only F31 is placed below the cyclopentadienyl ring plane due to its weak interaction with the adjacent titanium atom; the distance F31. ••Ti5 is 2.974(2) Å [3.037(2) Å]. The pentacoordinate Ti1 atom has the sum of F-Ti-F angles of 329°, whereas hexacoordinate Ti2, Ti3, and Ti4 atoms have a corresponding parameter (sum of the angles generated by four equatorial fluorine atoms) in the range 346-349°. Titanium atom Ti5 with the sum of the F-Ti-F angles of 335° represents an intermediate between hexa- and pentacoordinate Ti atoms. The shortest observed metal-metal separations Ti1...Ti2 and Ti3...Ti4 were found to be 3.3100(7) and 3.3039(6) Å, respectively [3.3083(7) and 3.3061(6) Å].

Polymerization of Styrene. Styrene polymerizations with half-sandwich titanium(IV) complexes 7-13 as catalysts and methylaluminoxane (MAO) as cocatalyst were carried out in toluene solution at 50 °C. The polymerization results together with data for reference complex CpTiCl<sub>3</sub> are summarized in Table 3. Under the given reaction conditions halosilyl-substituted complexes 7-12 exhibited catalytic activity comparable to that of CpTiCl<sub>3</sub>. Most of the monomer was converted to polystyrene (PS). All polystyrenes prepared with 7-12/MAO systems are significantly more stereoregular than that obtained using the reference CpTiCl<sub>3</sub>/MAO system, as expressed by a >10 °C increase in melting temperature of the PS. Observed melting points were in the range 264-267 °C and reflect the polymer crystallinity rather than their molecular weight. The polymers soluble in 1,2,4-trichlorobenzene were characterized by sizeexclusion chromatography (SEC). The molecular weights of the prepared PS were in the range reported for those for which other half-metallocene catalysts had been used under similar conditions.<sup>20</sup> An introduction of a halosilyl group on the cyclopentadienyl ring led to an increase of the PS molar mass in comparison with CpTiCl<sub>3</sub>, probably due to steric effects. In addition, silicon-bonded halide atoms can interact with bulky methylaluminoxane oligomers, producing greater hindrance at the cyclopentadienyl ligand.14 The PS obtained when fluorosilyl-

<sup>(19)</sup> Sotoodeh, M.; Leichtweis, I.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. Chem. Ber. 1993, 126, 913-919.

<sup>(20) (</sup>a) Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356–3360. (b) Kaminsky, W.; Scholz, V.; Werner, R. *Macromol. Symp.* **2000**, *159*, 9–17. (c) Kaminsky, W.; Lenk, S.; Scholz, V.; Roesky, H. W.; Herzog, A. *Macromolecules* **1997**, *30*, 7647–7650.



Figure 2. ORTEP style plot of the pentameric core of 13 at the 30% probability level. Circles labeled Cg1–Cg5 denote substituted cyclopentadienyl rings defined by carbons C11–C15, C21–C25, C31–C35, C41–C45, and C51–C55, respectively.



Figure 3. View of the molecular structure of 13 with the atom-labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. Orientation of the pentameric molecule is in accordance with Figure 2. H atoms are omitted for clarity.

substituted complexes were used had higher molar mass than the PS prepared using analogous chlorosilyl-substituted derivatives (compare catalysts 7 and 10 in Table 3). Polystyrenes prepared using complexes 8, 9, and 12 could not be characterized by SEC due to their complete insolubility in 1,2,4trichlorobenzene, caused by their high molar mass together with their high stereoregularity. The relatively narrow molar mass distributions ( $M_w/M_n = 2.32 - 2.47$ ) imply that the polymer preparation involved single-site catalysts. In the series of tested catalysts, complex 13 had the lowest catalytic activity owing to its oligomeric nature. This complex contains coordinatively saturated titanium atoms that cannot act as active sites. Styrene polymerizations catalyzed by 13 were performed at different Al/Ti ratios, and we established that the catalytic activity of this compound is not significantly dependent on MAO concentration, in contrast with the parent CpTiF<sub>3</sub>/MAO system.<sup>20</sup>

#### Summary

In this work, we have described the reactions of chlorosilylsubstituted cyclopentadienes and the corresponding cyclopentadienyl titanium(IV) trichlorides with Me<sub>3</sub>SnF, which gave novel fluorosilyl-substituted compounds. In the case of complexes  $[\text{TiCl}_3(\eta^5\text{-}C_5\text{H}_4\text{SiMe}_{(3-x)}\text{Cl}_x)]$ , where x = 1-3, the fluorination was very selective, giving compounds of the type  $[\text{TiCl}_3(\eta^5\text{-}C_5\text{H}_4\text{SiMe}_{(3-x)}F_x)]$ . Further fluorination with Me<sub>3</sub>SnF gave oligomeric and polymeric products of general formula  $[\text{TiF}_3(\eta^5\text{-}C_5\text{H}_4\text{SiMe}_{(3-x)}F_x)]$ , where x = 1-3. Electronic and  $^{47,49}\text{Ti}$  NMR spectroscopy showed the electron-withdrawing properties of the trihalosilyl substituent, whereas dihalo(methyl)-silyl and halo(dimethyl)silyl groups showed electron-donating features. All studied half-sandwich titanium complexes have catalytic activity in styrene polymerization, giving polystyrenes with significantly higher molecular weight and crystallinity than those prepared with reference compound CpTiCl<sub>3</sub>.

#### **Experimental Section**

**Materials.** All manipulations were performed under an argon atmosphere using standard Schlenk and vacuum-line techniques. Solvents were dried and deoxygenated by common methods and distilled just before use.  $C_5H_5(SiMe_3)$ ,<sup>21</sup> CpTiCl<sub>3</sub>,<sup>22</sup> C<sub>5</sub>H<sub>4</sub>(SiMe<sub>2</sub>-

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<sup>(22)</sup> Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. J. Chem. Soc., Dalton Trans. 1980, 1156–1160.

Cl)SiMe<sub>3</sub>,<sup>10</sup> [TiCl<sub>3</sub>( $\eta^{5}$ -C<sub>3</sub>H<sub>4</sub>SiMe<sub>2</sub>Cl)],<sup>10</sup> C<sub>5</sub>H<sub>4</sub>(SiMeCl<sub>2</sub>)SiMe<sub>3</sub>,<sup>11</sup> and [TiCl<sub>3</sub>( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiMeCl<sub>2</sub>)]<sup>12</sup> were prepared by known procedures. Me<sub>3</sub>SnF was prepared according to the literature<sup>23</sup> and was sublimed at 110 °C/0.1 Pa before use. Bu<sub>3</sub>SnF, SiCl<sub>4</sub>, *n*-BuLi, and TiCl<sub>4</sub> were obtained commercially (Aldrich) and used without further purification.

**Methods.** NMR spectra were recorded on Bruker AMX 360 and Bruker 500 Avance spectrometers equipped with a 5 mm broadband probe at 300 K (solutions in CD<sub>2</sub>Cl<sub>2</sub>, CDCl<sub>3</sub>, or toluene-*d*<sub>8</sub>), and the chemical shifts were referenced to external TMS, CFCl<sub>3</sub>, and TiCl<sub>4</sub>, respectively. Electronic absorption spectra were obtained using a Hewlet-Packard 8453 spectrometer (solvent CH<sub>2</sub>Cl<sub>2</sub>;  $10^{-2}$ – $10^{-4}$  M solutions in a 2 cm cuvette). Infrared spectra were measured as Nujol mulls (KBr cuvette) or neat (NaCl cuvette) under an argon atmosphere on a Perkin-Elmer 684 spectrophotometer. Melting points of 7–13 were determined in argon-sealed capillaries using a Stuart SMP-3 melting point apparatus and are uncorrected. Elemental C, H analyses were carried out on a Fisions EA1108 microanalyzer.

**Crystallography.** The X-ray data for both crystals of **10** and **13** were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å), a graphite monochromator, and the  $\varphi$  and  $\omega$  scan mode. Data reductions were performed with DENZO-SMN.<sup>24</sup> The absorption was neglected. Structures were solved by direct methods (Sir92)<sup>25</sup> and refined by full matrix least-square based on  $F^2$  (SHELXL97).<sup>26</sup> All hydrogen atoms were positioned geometrically and refined on their parent carbon atoms, with C–H = 0.93 Å and  $U_{iso}(H) = 1.2U_{eq}(C)$  for cyclopentadienyl H atoms and C–H = 0.96 Å and  $U_{iso}(H) = 1.5U_{eq}(C)$  for methyl hydrogen atoms.

Polymerization Studies. Styrene polymerizations were carried out in a 100 mL thermostated glass reactor equipped with a magnetic stirrer under nitrogen atmosphere. Toluene was freshly distilled under vacuum from sodium benzophenone ketvl prior to use. Styrene (Aldrich) was dried over calcium hydride, vacuum distilled, and immediately used for polymerization runs. Toluene, styrene, and MAO (10 wt % in toluene from Crompton) were introduced into the reactor, the temperature was adjusted to 50 °C, and the polymerization was initiated by injection of the catalyst (freshly prepared toluene solution). The total volume of the polymerization mixture was 30 mL for each run. The polymerizations were performed for a 120 min period. After this time the reaction was quenched by the addition of sec-butanol, and to the resulting mixture was added methanolic HCl. Polystyrene was collected by filtration, washed with methanol (3  $\times$  50 mL), and dried in vacuum oven to a constant weight. The reproducibility of the amount of polymer was estimated to be  $\pm 5\%$ . Melting points of obtained polystyrenes were determined on DSC 2920 (TA Instruments) under a nitrogen atmosphere with a heating rate of 10 °C/min. Both molar masses and molar dispersities  $(M_w/M_n)$  of the polymers were determined by high-temperature SEC (Polymer Laboratories PL-GPC 220) equipped with RI and viscometric detectors in 1,2,4-trichlorobenzene at 160 °C against atactic PS standards. The tacticity of the PS could not be studied by NMR spectroscopy due to poor solubility of prepared polymers.

 $C_5H_4$ (SiCl<sub>3</sub>)SiMe<sub>3</sub> (3). Silicon tetrachloride (12.91 g, 76.0 mmol) was added at once to a suspension of Li[ $C_5H_4$ (SiMe<sub>3</sub>)] (10.96 g, 76.0 mmol) in 200 mL of hexane at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 24 h to

ensure completion of the reaction. After 24 h of stirring, the precipitated LiCl was allowed to settle and the supernatant liquid was filtered through the Celite. Solvent was removed under reduced pressure, yielding a yellow, oily residue. Distillation at 40 °C/1 Pa gave **3** as a colorless liquid (14.67 g, 54.0 mmol, 71% yield) that crystallized on cooling at -15 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.19 (s, 9H, SiMe<sub>3</sub>), 3.43 (s, sp<sup>3</sup>-C bonded proton, isomers), 6.68 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 7.01 (m, 2H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR:  $\delta$  –0.9 (s, SiMe<sub>3</sub>), 60.3 (s, C<sub>*ipso*</sub>), 132.5 (s, C<sub>5</sub>H<sub>4</sub>), 135.5 (s, C<sub>5</sub>H<sub>4</sub>). IR (neat, cm<sup>-1</sup>): 3111w, 3094w, 3070m, 2960s, 2902m, 1656br-m, 1466 m, 1411m, 1283m, 1254vs, 1121s, 1083m, 1047m, 976vs, 949s, 844br-vs, 739vs, 695m. Anal. Found: C, 35.78; H, 4.91. Calc for C<sub>8</sub>H<sub>13</sub>Cl<sub>3</sub>Si<sub>2</sub>: C, 35.36; H, 4.82.

C<sub>5</sub>H<sub>4</sub>(SiMe<sub>2</sub>F)SiMe<sub>3</sub> (4). To a solution of C<sub>5</sub>H<sub>4</sub>(SiMe<sub>2</sub>Cl)SiMe<sub>3</sub>, 1 (3.00 g, 13.0 mmol), in 30 mL of CH<sub>2</sub>Cl<sub>2</sub> was added Me<sub>3</sub>SnF (2.38 g, 13.0 mmol), and the reaction mixture was stirred at room temperature for 24 h. After removing volatiles under reduced pressure the resulting yellow oil was distilled at 50 °C/400 Pa to give 4 as a moisture-sensitive colorless liquid (1.56 g, 7.3 mmol, 56% yield). The <sup>1</sup>H NMR spectrum of **4** is in agreement with that reported<sup>15</sup> by Borisova et al. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.00 (s, 9H, SiMe<sub>3</sub>), 0.02 (d,  ${}^{3}J_{H-F} = 7.1$  Hz, 6H, SiMe<sub>2</sub>F), 6.54 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 6.78 (m, 2H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR:  $\delta$  -2.0 (d, <sup>2</sup>J<sub>C-F</sub> = 15.1 Hz, SiMe<sub>2</sub>F), -1.4 (s, SiMe<sub>3</sub>), 58.8 (d,  ${}^{2}J_{C-F} = 13.2$  Hz,  $C_{ipso}$ ), 132.7 (s, C<sub>5</sub>H<sub>4</sub>), 133.5 (s, C<sub>5</sub>H<sub>4</sub>). <sup>19</sup>F NMR:  $\delta$  -151.62 (sep, <sup>3</sup>J<sub>F-H</sub> = 6.8 Hz,  ${}^{1}J_{F-Si} = 290$  Hz, SiMe<sub>2</sub>F). IR (neat, cm<sup>-1</sup>): 3098w, 3083m, 3069w, 2961s, 2902m, 1656br-m, 1431m, 1406m, 1285w, 1257vs, 1192w, 1122vs, 1078w, 1025m, 975vs, 921s, 876vs, 841s, 791s, 737vs, 691m, 660s, 625m. Anal. Found: C, 56.46; H, 9.21. Calc for C<sub>10</sub>H<sub>19</sub>FSi<sub>2</sub>: C, 56.01; H, 8.93.

**C**<sub>5</sub>**H**<sub>4</sub>(**SiMeF**<sub>2</sub>)**SiMe**<sub>3</sub> (5). Moisture-sensitive liquid 5 was prepared analogously from diene C<sub>5</sub>H<sub>4</sub>(SiMeCl<sub>2</sub>)SiMe<sub>3</sub> (2; 3.26 g, 13.0 mmol) and 2 equiv of Me<sub>3</sub>SnF. Distillation at 50 °C/670 Pa gave colorless 5 (1.79 g, 8.2 mmol, 63% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ -0.18 (t,  ${}^{3}J_{H-F} = 5.6$  Hz, 3H, SiMeF<sub>2</sub>), 0.08 (s, 9H, SiMe<sub>3</sub>), 6.64 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 6.93 (m, 2H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR: δ -8.7 (t,  ${}^{2}J_{C-F} = 17.6$  Hz, SiMeF<sub>2</sub>), -1.8 (s, SiMe<sub>3</sub>), 57.7 (t,  ${}^{2}J_{C-F} = 14.0$  Hz,  $C_{ipso}$ ), 132.1 (s, C<sub>5</sub>H<sub>4</sub>), 134.1 (s, C<sub>5</sub>H<sub>4</sub>). <sup>19</sup>F NMR: δ -129.30 (q,  ${}^{3}J_{F-H} = 5.4$  Hz,  ${}^{1}J_{F-Si} = 298$  Hz, SiMeF<sub>2</sub>). IR (neat, cm<sup>-1</sup>): 3101w, 3088m, 3070w, 2962m, 2911m, 1654br-m, 1407br-m, 1267s, 1253vs, 1125s, 1026m, 984s, 906s, 878vs, 828s, 744vs, 705m, 627m. Anal. Found: C, 49.96; H, 7.58. Calc for C<sub>9</sub>H<sub>16</sub>F<sub>2</sub>Si<sub>2</sub>: C, 49.50; H, 7.38.

**C**<sub>5</sub>**H**<sub>4</sub>(**SiF**<sub>3</sub>)**SiMe**<sub>3</sub> (6). Neat **3** (1.36 g, 5 mmol) was added to 4.64 g (15 mmol) of solid Bu<sub>3</sub>SnF, and the suspension was stirred until all of the Bu<sub>3</sub>SnF had dissolved (reaction was rather exothermic). The product was removed from the reaction mixture at 670 Pa to a trap cooled to −80 °C, leaving an oily residue of Bu<sub>3</sub>SnCl. Subsequent distillation of the crude product at 36 °C/ 670 Pa gave 0.47 g of colorless liquid 6 (yield 42%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.14 (s, 9H, SiMe<sub>3</sub>), 6.67 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 7.02 (m, 2H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR: −2.2 (s, SiMe<sub>3</sub>), 50.6 (q, <sup>2</sup>*J*<sub>C</sub>−*F* = 14.4 Hz, *C*<sub>*ipso*</sub>), 130.3 (s, C<sub>5</sub>H<sub>4</sub>), 134.9 (s, C<sub>5</sub>H<sub>4</sub>). <sup>19</sup>F NMR:  $\delta$  −138.44 (s, <sup>1</sup>*J*<sub>F−Si</sub> = 281 Hz, SiF<sub>3</sub>). IR (neat, cm<sup>-1</sup>): 3104m, 3087m, 2965s, 1656br-m, 1436m, 1266vs, 1114m, 1028m, 1001m, 949s, 896m, 846m, 812m, 743vs, 706s, 667m. Anal. Found: C, 43.68; H, 6.14. Calc for C<sub>8</sub>H<sub>13</sub>F<sub>3</sub>Si<sub>2</sub>: C, 43.21; H, 5.89.

[TiCl<sub>3</sub>( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>Cl)] (7). Compound 7 was prepared according to the published procedure<sup>10</sup> and purified by repeated sublimation at 70 °C/1 Pa. Mp: 83 °C. IR (Nujol mull, cm<sup>-1</sup>): 3112m, 3096m, 3087m, 1408s, 1369s, 1315m, 1262vs, 1182s, 1071m, 1049s, 960vs, 913m, 896s, 839vs, 795vs, 685s, 628s, 504s, 457vs, 426vs, 360m. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm): 398, 289, 246.

[TiCl<sub>3</sub>( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiMeCl<sub>2</sub>)] (8). Compound 8 was prepared according to the literature<sup>12</sup> and purified by repeated sublimation at 70 °C/1 Pa. Mp: 92 °C. IR (Nujol mull, cm<sup>-1</sup>): 3112m, 3098m, 3086m, 1409s, 1370s, 1316m, 1261s, 1189s, 1071m, 1048s, 914m,

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<sup>(24)</sup> Otwinowski, Z.; Minor, W. Methods Enzymol. 1997, 276, 307-326.

<sup>(25)</sup> Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. J. Appl. Crystallogr. **1993**, *26*, 343–350.

<sup>(26)</sup> Sheldrick, G. M. SHELXL-97; University of Göttingen: Göttingen, 1997.

895m, 844vs, 796vs, 748s, 626s, 565vs, 525vs, 458s, 424vs, 354m. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm): 391, 286, 246.

[TiCl<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiCl<sub>3</sub>)] (9). A solution of TiCl<sub>4</sub> (4.17 g, 22.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was cooled to -80 °C, and diene 3 (5.98 g, 22.0 mmol) was added at once. The reaction mixture was slowly warmed to room temperature, stirred for 12 h, and finally heated at reflux for 3 h to ensure complete reaction. Volatiles were removed under vacuum to give an orange residue, which was crystallized from hexane (20 mL). The crystals obtained on cooling of the orange filtrate to -80 °C were subsequently sublimed at 70 °C/1 Pa, yielding 9 as a yellow solid (5.12 g, 14.5 mmol, 66% yield). Mp: 99 °C. <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>): δ 6.14 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 6.56 (m, 2H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 126.0 (s, C<sub>5</sub>H<sub>4</sub>), 126.6 (s, Cipso), 128.2 (s, C5H4). IR (Nujol mull, cm<sup>-1</sup>): 3112m, 3100m, 3086m, 1411s, 1369s, 1318m, 1193s, 1072m, 1048vs, 913m, 843vs, 630s, 612vs, 597vs, 553vs, 457s, 430vs, 384m. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm): 377, 284sh, 246. Anal. Found: C, 17.24; H, 1.21. Calc for C<sub>5</sub>H<sub>4</sub>Cl<sub>6</sub>SiTi: C, 17.02; H, 1.14.

[TiCl<sub>3</sub>( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>F)] (10). Method A. The diene 4 (1.29 g, 6.0 mmol) was added at once to a solution of TiCl<sub>4</sub> (1.14 g, 6.0 mmol) in 40 mL of toluene at -20 °C. The reaction mixture was slowly warmed to room temperature and stirred for 16 h in the dark. After evaporation of volatiles under vacuum, the yellow residue was dissolved in hot hexane (25 mL), filtered through glass wool, and cooled to -80 °C, giving a microcrystalline solid. The isolated crystals were purified by sublimation at 40 °C/1 Pa, yielding yellow 10 (0.69 g, 2.8 mmol, 47% yield). Vacuum sublimation in a sealed ampule gave crystals of 10 suitable for X-ray crystal-lographic analysis.

**Method B.** Complex 7 (0.94 g, 3.0 mmol) was dissolved in toluene (25 mL), 1 equiv of Me<sub>3</sub>SnF (0.55 g, 3.0 mmol) was added, and the mixture was stirred in the dark for 24 h at room temperature. Solvent and Me<sub>3</sub>SnCl were removed under vacuum, and the yellow residue was purified as described above. Yield: 0.39 g (1.59 mmol, 53% yield). Mp: 69 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 0.62 (d, <sup>3</sup>*J*<sub>H-F</sub> = 7.3 Hz, 6H, SiMe<sub>2</sub>F), 7.17 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 7.37 (m, 2H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR:  $\delta$  -0.5 (d, <sup>2</sup>*J*<sub>C-F</sub> = 14.9 Hz, SiMe<sub>2</sub>F), 127.7 (s, C<sub>5</sub>H<sub>4</sub>), 130.3 (s, C<sub>5</sub>H<sub>4</sub>), 135.7 (d, <sup>2</sup>*J*<sub>C-F</sub> = 20.5 Hz, C<sub>*ipso*</sub>). <sup>19</sup>F NMR:  $\delta$  -155.21 (sep. <sup>3</sup>*J*<sub>F-H</sub> = 7.5 Hz, <sup>1</sup>*J*<sub>F-Si</sub> = 282 Hz, SiMe<sub>2</sub>F). IR (Nujol mull, cm<sup>-1</sup>): 3098m, 3088m, 1412s, 1315m, 1257vs, 1183s, 1049vs, 921m, 899s, 872vs, 843vvs, 827vs, 806vs, 774m, 666s, 631m, 461s, 430vs, 416vs, 360m. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm): 396, 283, 243. Anal. Found: C, 28.71; H, 3.43. Calc for C<sub>7</sub>H<sub>10</sub>Cl<sub>3</sub>FSiTi: C, 28.45; H, 3.41.

[TiCl<sub>3</sub>( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiMeF<sub>2</sub>)] (11). Method A. Yield: 0.99 g (3.30 mmol, 55%). Yellow crystalline 11 was purified by repeated sublimation at 50 °C/3 Pa.

**Method B.** Yield: 0.62 g (2.07 mmol, 69% yield). Mp: 61 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 0.76 (t,  ${}^{3}J_{H-F} = 6.1$  Hz, 3H, SiMeF<sub>2</sub>), 7.21 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 7.41 (m, 2H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR: δ -3.6 (t,  ${}^{2}J_{C-F} = 15.3$  Hz, SiMeF<sub>2</sub>), 126.7 (t,  ${}^{2}J_{C-F} = 23.7$  Hz, C<sub>ipso</sub>), 127.3 (s, C<sub>5</sub>H<sub>4</sub>), 130.2 (s, C<sub>5</sub>H<sub>4</sub>). <sup>19</sup>F NMR: δ -131.52 (q,  ${}^{3}J_{F-H} = 6.2$  Hz,  ${}^{1}J_{F-Si}$  = 291 Hz, SiMeF<sub>2</sub>). IR (Nujol mull, cm<sup>-1</sup>): 3103m, 1409m, 1318w, 1272s, 1195s, 1050s, 972m, 915m, 877vs, 840vs, 787s, 769s, 720vs, 699s, 635m, 449s, 430s, 377m. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm): 382, 281, 244. Anal. Found: C, 24.33; H, 2.41. Calc for  $C_6H_7Cl_3F_2SiTi$ : C, 24.07; H, 2.36.

[TiCl<sub>3</sub>( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiF<sub>3</sub>)] (12). Method A. Yield: 0.95 g (3.12 mmol, 52%). Bright yellow 12 was purified by sublimation at 40 °C/1 Pa.

**Method B.** Yield: 0.52 g (1.71 mmol, 57% yield); benzene was used instead of toluene. Mp: 47 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.27 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 7.48 (m, 2H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  125.4 (s, C<sub>5</sub>H<sub>4</sub>), 129.2 (s, C<sub>5</sub>H<sub>4</sub>). <sup>19</sup>F NMR:  $\delta$  –135.57 (s, <sup>1</sup>J<sub>F-Si</sub> = 259 Hz, SiF<sub>3</sub>). IR (Nujol mull, cm<sup>-1</sup>): 3109br-m, 1418s, 1373s, 1328m, 1212vs, 1170s, 1053s, 1023m, 967br-s, 922s, 832vs, 775br-vs, 709s, 635s, 594m, 504vs, 454s, 425vs, 383s. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm): 362, 273sh, 241. Anal. Found: C, 19.56; H, 1.26. Calc for C<sub>4</sub>H<sub>4</sub>Cl<sub>3</sub>F<sub>3</sub>-SiTi: C, 19.72; H, 1.33.

 $[TiF_3(\eta^5-C_5H_4SiMe_2F)]$  (13). To a solution of 7 (1.12 g, 3.6 mmol) in toluene was added Me<sub>3</sub>SnF (2.63 g, 14.4 mmol), and the mixture was stirred at ambient temperature for 48 h. A change of color from yellow to orange was gradually observed. After evaporation of solvents, the orange solid was washed with 10 mL of cold pentane and dried in vacuum. The crude product was extracted with boiling hexane on a frit. Cooling of the light yellow extract to -80 °C gave an orange solid (0.84 g, 3.4 mmol, 94% yield), which was characterized as 13. Single crystals suitable for X-ray crystal structure determination were grown from a saturated toluene solution layered with a double volume of hexane at -30°C. Mp: 92 °C (dec). <sup>1</sup>H NMR (toluene- $d_8$ ):  $\delta$  0.37 (d, <sup>3</sup> $J_{H-F}$  = 6.0 Hz, 6H, SiMe<sub>2</sub>F), 6.27 (br-m, 2H, C<sub>5</sub>H<sub>4</sub>), 6.45 (br-m, 2H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR:  $\delta - 0.8$  (d,  ${}^{2}J_{C-F} = 14.7$  Hz, SiMe<sub>2</sub>F), 124–131 (br-m, C<sub>5</sub>H<sub>4</sub>). <sup>29</sup>Si NMR:  $\delta$  9.6 (d, <sup>1</sup>*J*<sub>Si-F</sub> = 277 Hz). <sup>19</sup>F NMR:  $\delta$ -155.64, -155.01, -130.40, 173.42. IR (Nujol mull, cm<sup>-1</sup>): 3127m, 1655m, 1534s, 1504vs, 1494vs, 1468s, 1386vs, 1270w, 1232w, 1141w, 1103m, 1081m, 1053s, 986vs, 934w, 831m, 784s, 694m, 625m, 555s. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm): 339sh, 246. Anal. Found: C, 34.27; H, 4.01. Calc for C<sub>7</sub>H<sub>10</sub>F<sub>4</sub>SiTi: C, 34.16; H, 4.09.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 634117 (10) and 634649 (13).

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**Supporting Information Available:** Crystallographic data for the structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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## Synthesis, characterization and styrene polymerization behavior of alkoxysilyl-substituted monocyclopentadienyltitanium(IV) complexes

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#### ABSTRACT

Trimethylsilylcyclopentadienes bearing alkoxysilyl functionality,  $C_5H_4$ (SiMe<sub>3</sub>)(SiMe<sub>2</sub>OR), where R is Me (**2**), *i*-Pr (**3**) and *t*-Bu (**4**), were prepared and characterized. Methoxy derivative **2** reacts with TiCl<sub>4</sub> giving unstable [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>OMe)Cl<sub>3</sub>] (**5**), which is slowly transformed to chlorosilyl complex [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>Cl)Cl<sub>3</sub>] (**6**) and a mixture of cyclopentadienyltitanium(IV) methoxides on heating. Fully alkoxylated derivatives of the type [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>OR)(OR)<sub>3</sub>] [R = Me (**7**), *i*-Pr (**8**), *t*-Bu (**9**)] and {Ti[ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe(OMe)<sub>2</sub>](OMe)<sub>3</sub>} (**10**), were synthesized in low-to-moderate yields from respective chlorosilylcyclopentadienyltitanium trichlorides. All prepared alkoxysilyl compounds were characterized by spectroscopic techniques including <sup>29</sup>Si NMR. Polymerization activity of **7**–**10** in the presence of methylaluminoxane was determined and compared with [TiCp(OMe)<sub>3</sub>] and corresponding trimethylsilylsubstituted compounds [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)(OR)<sub>3</sub>], where R is Me, *i*-Pr and *t*-Bu. The highest conversion of styrene has been observed in systems based on [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)(OMe)<sub>3</sub>], [TiCp(OMe)<sub>3</sub>] and [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)(OBu<sup>t</sup>)<sub>3</sub>], respectively. The new alkoxysilyl compounds **7**–**10** have significantly lower activity of 500–1800 kg of polystyrene/(mol Ti mol styrene h). All prepared polystyrenes showed both high melting point and high degree of syndiotacticity as determined by DSC and NMR measurements.

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#### 1. Introduction

Group 4 organometallic and coordination compounds are intensively studied due to their ability to homogeneously polymerize and co-polymerize various olefins [1–3]. Beside the most widespread plastics such as polyethylene and polypropylene these complexes can also afford technical materials with higher added value such as cyclic olefin copolymers or syndiotactic polystyrene (*s*-PS) [4–6]. Polystyrenes obtained using compounds of the formula Cp/TiX<sub>3</sub> (Cp' is substituted cyclopentadienyl and X is anionic ligand) activated with the excess of methylaluminoxane (MAO) show highly defined microstructure, tacticity and high melting points [3]. Researches dealing with the study of polymerization mechanism showed that highly active catalyst often contains bulky cyclopentadienyl ligand (e.g. Cp\*, Ind, Me<sub>3</sub>SiCp, PhCp or Bu<sup>t</sup>Cp) and alkyl, alkoxy, aryloxy or fluoride ligands bonded to the central metal atom [7–11]. It was also shown that the introduction of alkoxide or fluoride ligand into precatalyst molecule allows significant reduction of MAO content during the polymerization run [12,13]. Recently we have reported the new fluorosilyl-substituted cyclopentadienyltitanium(IV) complexes yielding *s*-PS with moderate molecular weight ( $M_w$  16,000– 65,000) and high melting point (264–267 °C) [14].

Herein, we describe the synthesis and spectroscopic characterization of novel monocyclopentadienyltitanium(IV) complexes bearing alkoxy(dimethyl)silyl- and dimethoxy(methyl)silyl-substituted cyclopentadienyl ring. Catalytic behavior of prepared cyclopentadienyltitanium alkoxides in the syndiospecific polymerization of styrene is described. The solid-state structure of chlorosilyl complex [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>Cl)Cl<sub>3</sub>] is also reported.

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#### 2. Experimental section

#### 2.1. Materials and methods

Disubstituted cyclopentadiene **1** was synthesized following method of Ciruelos et al. [15]. The half-sandwich titanium(IV) complexes [TiCl<sub>3</sub>( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)], [TiCl<sub>3</sub>( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMeCl<sub>2</sub>)] and **6** were prepared by previously published procedures and purified by vacuum sublimation [14,16,17]. Alkoxide derivatives [TiCp(OMe)<sub>3</sub>], [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)(OR)<sub>3</sub>] (R = Me or *i*-Pr), **7**, **8** and **10** were synthesized from corresponding chloride derivatives according to known procedures [7,18]. Identity and purity of prepared compounds have been checked by multinuclear NMR spectroscopy. All preparative reactions and manipulations were carried out under inert atmosphere of argon on a Schlenk line. All solvents used for spectroscopic measurements were spectroscopic grade and dried over appropriate drying agents, distilled under argon and degassed before use.

#### 2.2. Spectroscopic measurements

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of trimethylsilylcyclopentadienes bearing alkoxysilyl functionality and alkoxysilyl-substituted monocyclopentadienyl-titanium(IV) complexes were recorded at 300 K on a Bruker Avance 500 NMR spectrometer at 500.13 and 126.76 MHz, respectively. The samples were dissolved in deuteriochloroform. The <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced to internal (CH<sub>3</sub>)<sub>4</sub>Si ( $\delta = 0.0$ ). The <sup>29</sup>Si NMR spectra were measured on a Bruker AVANCE II 400 NMR spectrometer at 79.49 MHz, The chemical shifts were referenced to external neat (CH<sub>3</sub>)<sub>4</sub>Si ( $\delta = 0.0$ ). IR spectra were recorded in 4000–350 cm<sup>-1</sup> region on a Nicolet 6700 FTIR spectrometer. Elemental analyses were carried out on a Fisons EA 1108 microanalyzer. Electronic absorption spectra were run on a Hewlett-Packard 8453 spectrometer with diode array (solvent *n*-hexane; 10<sup>-4</sup>–10<sup>-6</sup> M solutions in 1-cm quartz cuvette).

#### 2.3. Crystal structure determination

The X-ray data for 6 were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo  $K_{\alpha}$  radiation ( $\lambda~=~0.71073$  Å), a graphite monochromator, and the  $\phi$  and  $\omega$  scan mode. Data reductions were performed with DENZO-SMN [19]. The absorption was neglected. Structures were solved by direct methods (Sir92) [20] and refined by full matrix least-square based on  $F^2$  (SHELXL97) [21]. All hydrogen atoms were positioned geometrically and refined on their parent carbon atoms, with C-H = 0.93 Å and  $U_{iso}(H) = 1.2$  $U_{eq}(C)$  for cyclopentadienyl H atoms, and C-H = 0.96 Å and  $U_{iso}(H) = 1.5 U_{eq}(C)$  for methyl hydrogen atoms.  $R_{int} = \sum |F_o^2|$  $-F_{0,\text{mean}}^2 |\sum F_0^2$ , GOF =  $[\sum (w(F_0^2 - F_c^2)^2) / (N_{\text{diffrs}} - N_{\text{params}})]^{1/2}$  for all data,  $R(F) = \sum ||F_0| - |F_c| |\sum |F_0|$  for observed data,  $wR(F^2) = \left[\sum (w(F_0^2 - F_c^2)^2) / (\sum w(F_0^2)^2)\right]^{1/2}$  for all data. Crystals of **6** suitable for X-ray crystallographic analysis were grown by the sublimation of 5 in sealed ampoule at 40 °C and 0.1 Pa. Crystallographic data for **6**:  $C_7H_{10}Cl_4SiTi$ , M = 311.94, triclinic, *P*-1, a =6.5750(3), b = 6.7451(2), c = 15.8159(5) Å,  $\alpha = 79.732(3)$ ,  $\beta =$ 89.774(4),  $\gamma = 63.735(3)^{\circ}$ , Z = 2, V = 616.69(4) Å<sup>3</sup>,  $D_c = 1.680$  g cm<sup>-3</sup>,  $\mu = 1.611 \text{ mm}^{-1}, T_{\min}/T_{\max} = 0.604/0.917; -8 \le h \le 8,$  $-8 \le k \le 8, -20 \le l \le 20; 10,467$  reflections measured ( $\theta_{max} = 27.5^{\circ}$ ), 10,428 independent ( $R_{int} = 0.0299$ ), 2450 with  $I > 2\sigma(I)$ , 118 parameters, S = 1.147,  $R_1$ (obs. data) = 0.0289,  $wR_2 = 0.0678$ ; max., min. residual electron density = 0.422, -0.402 e Å<sup>-3</sup>.

#### 2.4. Polymerization procedures

Polymerizations were performed in 100 ml double-walled glass magnetically stirred reactor. Toluene was refluxed with sodium and distilled under nitrogen prior to use. Styrene monomer (Synthos, polymerization grade) was dried over calcium hydride, vacuum distilled, and immediately used for polymerization runs. Toluene, styrene, and MAO (10 wt.% in toluene from Aldrich) were introduced into the reactor and tempered to desired reaction temperature for 15–20 min. Polymerization was then started by injection of toluene catalyst solution. The polymerization was quenched after 60 min by the addition of 2 ml of EtOH/HCl. Polystyrene was precipitated in large excess of EtOH with 2% of HCl, filtered, washed with ethanol and dried in vacuum oven at 50 °C to a constant weight.

#### 2.5. Characterization of prepared polystyrenes

DSC measurements were performed on a TA Instrument module Q100 at a rate of 10 °C min<sup>-1</sup> for both heating and cooling. Samples were heated to 300 °C, kept isothermally for 5 min, cooled to 150 °C and heated again to 300 °C. Heat of the fusion 53.2 J g<sup>-1</sup> for hypothetical 100% crystalline *s*-PS was used to calculate the degree of crystallinity [22–24]. The syndiotacticity of polystyrenes was determined by <sup>13</sup>C NMR spectroscopy in  $C_6D_6/1,2,4$ -trichlorbenzene (10/90 v/v) solution at 120 °C on a 500 MHz Bruker Avance DRX 500 spectrometer using INVGATE pulse sequence, 10 s relaxation delay and 2000–5000 scans to ensure quantitative spectra. Spectra were assigned and quantitatively analyzed as described elsewhere [25,26].

#### 2.6. Synthesis of studied compounds

#### 2.6.1. $C_5H_4(SiMe_3)(SiMe_2OMe)$ (2)

To a solution of C<sub>5</sub>H<sub>4</sub>(SiMe<sub>3</sub>)(SiMe<sub>2</sub>Cl) (9.24 g, 40 mmol) in 80 ml of Et<sub>2</sub>O was added mixture of 8.35 ml (60 mmol) Et<sub>3</sub>N and 2.43 ml (60 mmol) MeOH at 0 °C. Dense mixture was stirred for 1 day at room temperature. Precipitate of Et<sub>3</sub>NHCl has been filtered off, washed with 3  $\times$  20 ml of Et<sub>2</sub>O and filtrate was evaporated in vacuum. Resulting yellow liquid was purified by distillation (50-51 °C, 5 mm Hg) on a short Vigreux column yielding 5.33 g (59%) of **2** as colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): -0.09 (s, 6H), -0.04 (s, 9H), 3.39 (s, 3H), 6.53 (m, 2H), 6.70 (m, 2H). <sup>13</sup>C NMR: -2.8, -1.1, 50.7, 60.1, 131.3, 134.8. <sup>29</sup>Si NMR: 9.8 (SiMe<sub>2</sub>OMe), -1.9 (SiMe<sub>3</sub>). MS [m/z (%)]: 226 (30), M<sup>+</sup>; 211 (100), M<sup>+</sup> – Me; 195 (40), M<sup>+</sup> – OMe; 122 (49), M<sup>+</sup> – Me<sub>3</sub>SiOMe; 89 (33), Me<sub>2</sub>SiOMe<sup>+</sup>; 73 (43), Me<sub>3</sub>Si<sup>+</sup>, 59 (28). IR (cm<sup>-1</sup>): 3081m (*v*<sub>CH</sub> unsaturated), 2955s, 2901m, 2832m, ( $\nu_{CH}$  aliphatic) 1649m ( $\nu_{C}$ =<sub>C</sub>), 1248vs ( $\delta_{CH}$  in SiCH<sub>3</sub> moiety), 1091vs (*v*<sub>SiO</sub>). UV-vis [maxima at (nm)]: 198, 227, 275sh. Anal. Calc. for C<sub>11</sub>H<sub>22</sub>OSi<sub>2</sub>: C, 58.34; H, 9.79. Found: C, 58.32; H, 9.80.

#### 2.6.2. $C_5H_4(SiMe_3)(SiMe_2OPr^i)$ (3)

The operation was the same as that described for **2**.  $C_5H_4$ (Si-Me<sub>3</sub>)(SiMe<sub>2</sub>Cl) (2.07 g, 9 mmol), Et<sub>3</sub>N (12.6 ml, 90 mmol) and *i*-PrOH (6.9 ml, 90 mmol) reacted for 3 days to give 1.25 g (55% yield) of colorless oil (58–62 °C, 5 mm Hg). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): -0.06 (s, 6H), 0.01 (s, 9H), 1.16 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.0 Hz, 6H), 3.97 (sep, <sup>3</sup>*J*<sub>HH</sub> = 6.0 Hz, 1H), 6.54 (m, 2H), 6.71 (m, 2H). <sup>13</sup>C NMR: -1.4, -0.8, 26.0, 65.4, 59.7, 131.0, 135.3. <sup>29</sup>Si NMR: 5.1 (SiMe<sub>2</sub>OCH(Me)<sub>2</sub>), -2.0 (SiMe<sub>3</sub>). MS [*m*/*z* (%)]: 255 (62), M<sup>+</sup>; 239 (58), M<sup>+</sup> – Me; 196 (100), M<sup>+</sup> – OPr; 147 (51), 122 (22), M<sup>+</sup> – Me<sub>3</sub>SiOPr; 118 (97), Me<sub>2</sub>SiOPr<sup>+</sup>; 73 (60), Me<sub>3</sub>Si<sup>+</sup>, 43 (23), Pr<sup>+</sup>. IR (cm<sup>-1</sup>): 3081m ( $\nu$ <sub>CH</sub> unsaturated), 2965s, 2957s, 2926m, 2899m, 2874m, ( $\nu$ <sub>CH</sub> aliphatic), 1649m ( $\nu$ <sub>C=C</sub>), 1249vs ( $\delta$ <sub>CH</sub> in SiCH<sub>3</sub> moiety), 1023vs ( $\nu$ <sub>SiO</sub>). UV–vis

[maxima at (nm)]: 193, 230, 269sh. Anal. Calc. for C<sub>13</sub>H<sub>26</sub>OSi<sub>2</sub>: C, 61.35; H, 10.30. Found: C, 61.30; H, 10.26.

Anal. Calc. for C<sub>19</sub>H<sub>38</sub>O<sub>4</sub>SiTi: C, 56.14; H, 9.42. Found: C, 56.02; H, 9.31.

#### 2.6.3. $C_5H_4(SiMe_3)(SiMe_2OBu^t)$ (4)

To a solution of  $C_5H_4(SiMe_3)(SiMe_2Cl)(3.46 g, 15 mmol)$  in 50 ml THF was dropwise added t-BuOK (1.68 g, 15 mmol) dissolved in 15 ml THF at 0 °C. After slow warming to room temperature the mixture was stirred for additional 12 h. THF was evaporated and resulting waxy solid was purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>/hexane). After vacuum evaporation of solvent 0.48 g (12% yield) of **4** was obtained. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): -0.05 (s, 6H), 0.00 (s, 9H), 1.31 (s, 9H), 3.71 (s, sp<sup>3</sup>-C bonded proton, isomers), 6.54 (m, 2H), 6.70 (m, 2H). <sup>13</sup>C NMR: -1.8, 0.8, 18.9, 31.8, 59.4, 130.4, and 135.5. <sup>29</sup>Si NMR: 2.3, 0.6, -0.6, -1.4, -2.6, -11.0 (mixture of isomers). MS [*m*/*z* (%)]: 269 (8), M<sup>+</sup>; 212 (2), M<sup>+</sup> – Bu; 132 (21), Me<sub>2</sub>SiOBu<sup>+</sup>; 122 (52), M<sup>+</sup> – Me<sub>3</sub>SiOBu; 73 (100), Me<sub>3</sub>Si<sup>+</sup>, 57 (86), Bu<sup>+</sup>. IR (cm<sup>-1</sup>): 3081m (*v*<sub>CH</sub> unsaturated), 2967m, 2957s, 2926m, 2900m, 2874m, ( $\nu_{CH}$  aliphatic), 1650m ( $\nu_{C}$ =<sub>C</sub>), 1248vs ( $\delta_{CH}$  in SiCH<sub>3</sub> moiety), 1044vs (v<sub>SiO</sub>). UV-vis [maxima at (nm)]: 194, 246sh, 300sh. Anal. Calc. for C<sub>14</sub>H<sub>28</sub>OSi<sub>2</sub>: C, 62.62; H, 10.51. Found: C, 62.85; H, 10.67.

#### 2.6.4. $[Ti(\eta^5 - C_5H_4SiMe_2OMe)Cl_3]$ (5)

To a solution of TiCl<sub>4</sub> (4.17 g, 22.0 mmol) in toluene (50 ml) cooled to 0 °C the diene **2** (6.60 g, 30.0 mmol) was added at once. The reaction mixture was slowly warmed to room temperature, stirred for 12 h and volatiles were removed under vacuum. Waxy greenish-yellow residue was crystallized from hexane at -40 °C giving 0.57 g of solid, which was characterized as a mixture of silyl-substituted cyclopentadienyltitanium(IV) compounds, see the Section 3.2. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 0.17 [s, Si(CH<sub>3</sub>)<sub>2</sub>OMe], 0.83 [s, Si(CH<sub>3</sub>)<sub>2</sub>Cl], 4.69 (br-s, SiMe<sub>2</sub>OCH<sub>3</sub>), 5.34 (s, TiOCH<sub>3</sub>), 7.14 (m, C<sub>5</sub>H<sub>4</sub>R), 7.37 (m, C<sub>5</sub>H<sub>4</sub>R). <sup>13</sup>C NMR: -6.6 [Si(CH<sub>3</sub>)<sub>2</sub>OMe], 2.6 [Si(CH<sub>3</sub>)<sub>2</sub>Cl], 57.0 [br, SiMe<sub>2</sub>OCH<sub>3</sub>], 66.1 (TiOCH<sub>3</sub>), 125.5, 126.5, 126.9, 129.7, 130.3 (C<sub>ipso</sub>), 135.4 (C<sub>ipso</sub>). IR (cm<sup>-1</sup>): 3108m, 3093m ( $\nu_{CH}$  aromatic), 2960s, 2902m ( $\nu_{CH}$  aliphatic), 1255vs ( $\delta_{CH}$  in SiCH<sub>3</sub> moiety), 1098vs ( $\nu_{SiO}$ ).

#### 2.6.5. $[Ti(\eta^5 - C_5 H_4 SiMe_2 OMe)(OMe)_3]$ (7)

0.95 g (3.04 mmol) of **6** was dissolved in 50 ml of Et<sub>2</sub>O and the mixture NEt<sub>3</sub> (2.09 ml, 15 mmol) with MeOH (0.6 ml, 15 mmol) in 15 ml of ether has been added. Resulting suspension was stirred for 1 day at room temperature. Precipitate was filtered off, washed with Et<sub>2</sub>O and filtrate was evaporated in vacuum yielding light yellow oil. After vacuum distillation (65 °C/5 Pa) on Kugelrohr apparatus, 230 mg (yield 26%) colorless oil obtained. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 0.11 (s, 6H), 3.16 (s, 3H), 3.80 (s, 9H), 6.18 (m, 2H), 6.32 (s, 2H). <sup>13</sup>C NMR: -2.5, 49.7, 64.1, 115.5, 120.4, 121.3. <sup>29</sup>Si NMR: 5.4. IR (cm<sup>-1</sup>): 3081m ( $\nu_{CH}$  aromatic), 2909s, 2806vs ( $\nu_{CH}$  aliphatic), 1251vs ( $\delta_{CH}$  in SiCH<sub>3</sub> moiety), 1081vs ( $\nu_{SiO}$ ), 553vs ( $\nu_{TiO}$ ). UV–vis [maxima at (nm)]: 214sh, 249sh, 305. Anal. Calc. for C<sub>11</sub>H<sub>22</sub>O<sub>4</sub>SiTi: C, 44.90; H, 7.54. Found: C, 44.75; H, 7.61.

#### 2.6.6. $[Ti(\eta^5 - C_5H_4SiMe_2OPr^i)(OPr^i)_3]$ (8)

From the **6** (1.14 g, 3.66 mmol), NEt<sub>3</sub> (10.2 ml, 73 mmol) and *i*-PrOH (5.58 ml, 73 mmol) in 70 ml of ether crude **8** has been prepared following the method described for **7**. After vacuum distillation of pale yellow oil on Kugelrohr apparatus at 60–65 °C/ 1 Pa, 190 mg (yield 13%) of pure **8** was isolated. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 0.34 (s, 6H), 1.06 (d, <sup>3</sup>J<sub>HH</sub> = 6.1 Hz, 18H), 1.19 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 6H), 3.93 (sep, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 1H), 4.46 (sep, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 3H), 6.29 (m, 2H), 6.48 (s, 2H). <sup>13</sup>C NMR: -0.7, 26.0, 26.7, 65.0, 76.4, 114.0, 120.4, 121.6. <sup>29</sup>Si NMR: -1.5. IR (cm<sup>-1</sup>): 3089w ( $\nu_{CH}$  aromatic), 2967vs, 2929m, 2863m ( $\nu_{CH}$  aliphatic), 1250s ( $\delta_{CH}$  in SiCH<sub>3</sub> moiety), 1019vs ( $\nu_{SiO}$ ), 594vs ( $\nu_{TiO}$ ). UV–vis [maxima at (nm)]: 223, 320.

#### 2.6.7. $[Ti(\eta^5 - C_5H_4SiMe_2OBu^t)(OBu^t)_3]$ (**9**)

To the THF (50 ml) solution of **6** (1.00 g, 3.21 mmol) was added a THF (40 ml) solution of *t*-BuOK (1.44 g, 12.84 mmol) at 0 °C. Mixture was allowed to room temperature and stirred for additional 12 h. After evaporation of solvent in vacuum, waxy residue was extracted with hot hexane and filtered. Removing of solvent followed with vacuum distillation on Kugelrohr apparatus (130– 135 °C/10 Pa) yielded 560 mg (yield 12%) of **9** as pale yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 0.50 (s, 6H), 1.26 (s, 27H), 1.33 (s, 9H), 6.33 (m, 2H), 6.54 (s, 2H). <sup>13</sup>C NMR: 2.2, 32.1, 32.5, 62.3, 81.1, 112.1, 120.9, 121.5. <sup>29</sup>Si NMR: -5.7. IR (cm<sup>-1</sup>): 3095w ( $\nu_{CH}$  aromatic), 2971vs, 2929m, 2901m, 2870m ( $\nu_{CH}$  aliphatic), 1251vs ( $\delta_{CH}$  in SiCH<sub>3</sub> moiety), 1002vs ( $\nu_{SiO}$ ), 564vs ( $\nu_{TiO}$ ). UV–vis [maxima at (nm)]: 195, 226, 288. Anal. Calc. for C<sub>23</sub>H<sub>46</sub>O<sub>4</sub>SiTi: C, 59.72; H, 10.02. Found: C, 59.61; H, 10.20.

#### 2.6.8. $\{Ti[\eta^5 - C_5H_4SiMe(OMe)_2](OMe)_3\}$ (**10**)

1.66 g (5 mmol) of [TiCl<sub>3</sub>( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMeCl<sub>2</sub>)] was dissolved in 150 ml of Et<sub>2</sub>O and the mixture of NEt<sub>3</sub> (4.49 ml, 32 mmol) with MeOH (1.31 ml, 32 mmol) in 10 ml of Et<sub>2</sub>O was added at 0 °C. Resulting suspension was stirred for 1 day at RT, precipitate was filtered off, washed with Et<sub>2</sub>O and filtrate was evaporated in vacuum yielding light yellow oil. After vacuum distillation on Kugelrohr apparatus (70 °C/40 Pa), 404 mg (yield 26%) of colorless oil was obtained. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 0.30 (s, 3H), 3.49 (s, 6H), 4.02 (s, 9H), 6.38 (m, 2H), 6.57 (s, 2H). <sup>13</sup>C NMR: -4.7, 50.3, 65.0, 116.3, 117.7, 121.6. <sup>29</sup>Si NMR: -17.3. IR (cm<sup>-1</sup>): 3051w ( $\nu_{CH}$ aromatic), 2910s, 2887m, 2809s ( $\nu_{CH}$  aliphatic), 1256m ( $\delta_{CH}$  in SiCH<sub>3</sub> moiety), 1082s, 1037vs ( $\nu_{SiO}$ ), 540br,s ( $\nu_{TiO}$ ). UV–vis [maxima at (nm)]: 230sh, 253sh, 290sh. Anal. Calc. for C<sub>11</sub>H<sub>22</sub>O<sub>5</sub>SiTi: C, 42.58; H, 7.15. Found: C, 42.51; H, 7.21.

#### 2.6.9. $[Ti(\eta^5 - C_5H_4SiMe_3)(OBu^t)_3]$

1.53 g (5.2 mmol) of  $[Ti(\eta^5-C_5H_4SiMe_3)Cl_3]$ , NEt<sub>3</sub> (2.80 ml, 20 mmol) and *t*-BuOH (1.94 ml, 20 mmol) in 150 ml of Et<sub>2</sub>O were allowed to react for two days at RT. Following the method described for **7**, colorless oil (720 mg, yield 34%, b.p. 130 °C/50 Pa) has been obtained. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 0.36 (s, 9H), 1.32 (s, 27H), 6.39 (m, 2H), 6.52 (s, 2H). <sup>13</sup>C NMR: 0.2, 32.2, 81.0 (Bu<sup>t</sup>-ipso), 112.1, 120.7, 121.4 (Cp-ipso). <sup>29</sup>Si NMR: -8.9. IR (cm<sup>-1</sup>): 3096w ( $\nu_{CH}$  aromatic), 2971s, 2926m, 2898m, 2867m ( $\nu_{CH}$  aliphatic), 1247vs ( $\delta_{CH}$  in SiCH<sub>3</sub> moiety), 566m ( $\nu_{TiO}$ ). UV–vis [maxima at (nm)]: 222, 298sh. Anal. Calc. for C<sub>20</sub>H<sub>40</sub>O<sub>3</sub>SiTi: C, 59.38; H, 9.97. Found: C, 59.21; H, 10.09.

#### 3. Results and discussion

## 3.1. Synthesis and characterization of alkoxysilyl-substituted cyclopentadienes

The most common procedure for the preparation of complexes of the type [TiCp'Cl<sub>3</sub>] utilizes the reaction of substituted trimethylsilylcyclopentadiene (Cp'SiMe<sub>3</sub>) with titanium tetrachloride.


Thus at the first, our efforts were focused on the preparation and characterization of trimethylsilylcyclopentadienes **2–4** bearing alkoxysilyl group, see Scheme 1. The air-stable liquid **2** was synthesized from known chlorosilyl precursor  $C_5H_4(SiMe_3)(Si-Me_2Cl)$  (**1**) by its reaction with methanol in the presence of trie-thylamine. For the preparation of cyclopentadiene **3**, longer reaction times and large excess of *i*-PrOH/NEt<sub>3</sub> were required to ensure complete reaction. *Tert*-butoxy derivative **4** is not accessible by this method and *t*-BuOK in THF must be used.

Cyclopentadienes **2** and **3** were purified by vacuum distillation, but compound **4** decomposes on heating. The synthesis of dienes of the type  $C_5H_4(SiMe_3)[SiMe(OR)_2]$  and  $C_5H_4(SiMe_3)[Si(OR)_3]$ , where R is Me, *i*-Pr or *t*-Bu, was not successful and insoluble rubber-like compounds were obtained. In the IR spectra of these products the strong absorption bands in the region 1040–1060 cm<sup>-1</sup> corresponding to Si–O stretching were found, which is a characteristic for short-chain siloxanes [27].

The <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra of diene **2** are identical to those previously reported and prove that 2 is present exclusively as the 1,1isomer and is not fluxional at ambient temperature [28]. The NMR spectra of 3 and 4 are more complex and correspond to a mixture of isomers nevertheless; the signals of corresponding 1,1-isomers are dominant. The mass spectra of 2, 3 and 4 showed appropriate molecule peaks at m/z 226, 254 and 268, respectively. The most intense signals found in MS spectra correspond to elimination of methyl or alkoxyl group, respectively. Peak at m/z 122 present in all MS spectra is due to dimethylsilafulvene cation resulting from dissociation of ROSiMe<sub>3</sub> (R = Me, *i*-Pr or *t*-Bu) from the molecule of corresponding diene. Rozell and Jones have previously described this fragmentation pattern for compound 2 [28]. In the IR spectra of **2–4** the bands characteristic for allylic hydrogens ( $v_{CH}$  at 3120– 3080 cm<sup>-1</sup>), aliphatic C–H bonds ( $\nu_{CH}$  at 2980–2860 cm<sup>-1</sup>) and C=C bonds ( $\nu_{\rm C}$ =<sub>C</sub> at 1654–1656 cm<sup>-1</sup>) were observed. The sharp band at 1249 cm<sup>-1</sup> has been unambiguously assigned to the symmetric C-H deformation of methyl groups bonded to the silicon atom [29]. The Si–O stretching mode gives characteristic strong absorption band in the region  $1020-1090 \text{ cm}^{-1}$  [30].

# 3.2. Synthesis and characterization of cyclopentadienyltitanium(IV) complexes

Cyclopentadienes **3** and **4** bearing *i*-PrO and *t*-BuO group, respectively, quickly decompose in the presence of titanium



tetrachloride, even at low temperatures giving dark tarry materials. From the reaction of diene 2 with TiCl<sub>4</sub> small amount of yellow solid has been isolated (Scheme 2). This product was characterized as a mixture of monocyclopentadienyltitanium(IV) compounds containing methoxy group bonded to the silicon or titanium atom, respectively. In <sup>1</sup>H and <sup>13</sup>C NMR dominant signals (approx. 85–90%) corresponding to complex [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Si-Me<sub>2</sub>OMe)Cl<sub>3</sub>] (**5**) have been observed. The <sup>1</sup>H line of CH<sub>3</sub>OSi– substituent at 4.5–4.9 ppm (55–59 ppm in <sup>13</sup>C NMR) is significantly broadened and the signal of Si nucleus resonance in the <sup>29</sup>Si NMR spectrum was not detected probably also due to strong line broadening. Signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra at 0.83 ppm and 2.6 ppm, respectively, are due to presence of  $ClSi(CH_3)_2$  group. Methoxy group bonded to titanium atom gave  $^1\mathrm{H}$  and  $^{13}\mathrm{C}$  NMR singlets at 5.34 and 66.1 ppm, respectively. During the standing of **5** dissolved in CDCl<sub>3</sub> at ambient temperature and particularly after the heating to 50 °C, signals of CH<sub>3</sub>OSi slowly fade out and the resonances of CH<sub>3</sub>OTi fragment increase in intensity. These results are indicative for the migration of CH<sub>3</sub>O group from the silicon to the central titanium atom. On attempts to prepare crystals of 5 suitable for X-ray diffraction analysis by the sublimation in vacuum sealed ampoule, we have obtained yellow crystals characterized by spectroscopic methods and particularly by X-ray analysis as  $[Ti(\eta^5-C_5H_4SiMe_2Cl)Cl_3]$ , (6), and dark oily residue. In the <sup>1</sup>H NMR spectrum of this dark oil, signal of CH<sub>3</sub>OTi fragment at 5.33 ppm has been found, whereas the line of CH<sub>3</sub>OSiMe<sub>2</sub> substituent was not observed.

According to these observations, it is evident that migration of methoxy group from silicon to titanium atom is intermolecular process proceeding in both solution and gaseous state. Despite the fact that the Si–O bond dissociation enthalpy (123 kcal mol<sup>-1</sup> in Me<sub>3</sub>SiOMe) [31] is higher than that for Ti–O bond (109 kcal mol<sup>-1</sup> in tetraalkoxides) [32], the complex **5** is less stable than resulting methoxytitanium(IV) compounds. The enhanced strength of Ti–O bond could be attributed to  $\pi$ -interaction of oxygen lone pairs with empty *d*-orbitals of titanium. The shortening and strengthening of the Ti–O bond via this process is also known for bis(cyclopentadienyl) titanium(IV) complexes of [(TiCp<sub>2</sub>X)<sub>2</sub>O] and [TiCp<sub>2</sub>(OR)X] type (R = alkyl, X is halide or pseudohalide) [33–35].

Fully alkoxylated half-sandwich titanium(IV) complexes 7, 8 and **10** were prepared from their chloride congeners following the method described by Nesmeyanov et al. [18] The tert-butoxy compound **9** was synthesized using *t*-BuOK instead of alcohol/ NEt<sub>3</sub> mixture as shown in Scheme 3. Alkoxides 7–10 are moisturesensitive viscous oils that could be purified by vacuum distillation. Methoxy derivatives 7 and 10 solidify and partially crystallize during the storage below a temperature of 4 °C, probably due to oligomerization. Bridging ability of alkoxy function in various titanium complexes giving dimeric or oligomeric species is well described in literature [36–39]. The simple <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra of 7-10 affirmed the expected structure of cyclopentadienyltitanium(IV) alkoxylates and no dynamic or fluxional processes were observed in the solution at room temperature. The infrared spectra of 7-10 show bands of aromatic (3050-3100 cm<sup>-1</sup>) and aliphatic C–H stretching (2800–3000 cm<sup>-1</sup>). The strong absorptions of Si-O and Ti-O stretch have been observed in the region 1000–1100  $\text{cm}^{-1}$  and 550–580  $\text{cm}^{-1}$ , respectively.

#### 3.3. Molecular structure of 6

During the sublimation of methoxy derivative **5** we have isolated chlorosilyl complex **6** and its solid-state structure was analyzed by single-crystal X-ray diffraction. Fig. 1 shows molecular structure of **6** together with selected geometrical parameters, crystallographic data



are given in the Section 2.3. Molecule has the expected three-legged piano-stool configuration with distorted tetrahedral coordination of the titanium atom. The geometrical parameters are similar to those for related cyclopentadienyltitanium(IV) trichlorides [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Si-Me<sub>2</sub>F)Cl<sub>3</sub>] and [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Bu<sup>t</sup>)Cl<sub>3</sub>] [14,40]. The steric influence of bulky substituent bonded to the Cp ring causes slightly larger Cg–Ti–Cl angle observed for chlorine atoms adjacent to chlorosilyl group. Silicon-bonded chlorine atom of the substituent is located below cyclopentadienyl ring plane, toward the titanium center. The dihedral angle between the cyclopentadienyl ring plane and the C<sub>ipso</sub>–Si bond vector is 5.7(1)°.



**Fig. 1.** ORTEP drawing (50% probability) of **6**. Selected interatomic distances (Å) and angles (deg): Ti1–Cg1, 2.0135(13); Ti1–Cl1, 2.2254(7); Ti1–Cl2, 2.2273(7); Ti1–Cl3, 2.2304(7); Cg1–Ti1–Cl1, 117.19(4); Cg1–Ti1–Cl2, 116.02(4); Cg1–Ti1–Cl3, 114.67(4); Cl1–Ti1–Cl2, 103.09(3); Cl2–Ti1–Cl3, 102.54(4); Cl1–Ti1–Cl3, 101.15(3).

## 3.4. Polymerization results

The new complexes bearing alkoxysilyl functionality were tested for styrene polymerization in toluene at 50 °C and Al/ Ti = 500, i.e. conditions optimized for known catalyst [CpTi(OMe)<sub>3</sub>] to achieve high activity as well as high PS syndiotacticity [7]. For the purpose of comparison, the catalytic activity of corresponding trimethylsilyl-substituted derivatives  $[Ti(\eta^5-C_5H_4SiMe_3)(OR)_3]$ , where R is Me, *i*-Pr and *t*-Bu, was also examined. Polymerization results, together with characterization data of prepared polystyrenes are summarized in Table 1. The highest activity was observed for the complexes  $[Ti(\eta^5-C_5H_4SiMe_3)(OMe)_3]$ , [TiC $p(OMe)_3$  and  $[Ti(\eta^5-C_5H_4SiMe_3)(OBu^t)_3]$ , respectively. By contrast, the compounds with alkoxysilyl substituents (runs 1.5-1.8) showed significantly lower conversion of styrene. Nevertheless, the activity of 7-10 is still higher than those reported for other monocyclopentadienyltitanium(IV) compounds bearing oxygen atom in Cp-bonded functionality [41-44]. The decrease of catalytic activity by the introduction of alkoxysilyl group could be attributed to possible coordination of methylaluminoxane molecule via oxygen-aluminum bond. Since MAO is oligomeric compound, the interaction of cyclopentadienyl complex with MAO dramatically increases steric hindrance of catalytically active species resulting in lower polymerization activity. Intramolecular coordination  $0 \rightarrow Ti$ described in {Ti[ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)]Cl<sub>3</sub>} or [ $\eta^5$ -(2-tetrahydrofurfuryl)-cyclopentadienyl]titanium trichloride [43,44] is unlikely in 7-10 owing to unfavorable spatial disposition. Highly syndiotactic arrangement of phenyl groups in all prepared polystyrenes is evident from their high melting temperatures (268-270 °C) as measured by DSC. Typically, two melting endotherms were observed in second heating DSC run showing different arrangement of s-PS crystalline phase. The degree of stereoregularity of prepared polystyrenes was determined by means of quantitative <sup>13</sup>C NMR spectroscopy [45]. In both aliphatic CH<sub>2</sub> (43.0-46.5 ppm) and aromatic ipso-carbon (145-146 ppm) regions we have observed exclusively single peak of rrrrr hexad and rrrrrr heptad resonance, respectively. Since this method is able to detect concentration of meso defects within the accuracy better than 1%, polystyrenes prepared in runs 1.2–1.5, 1.7, and 1.8 are almost pure s-PS [25,45]. In the <sup>13</sup>C NMR spectrum of PS sample obtained using unsubstituted catalyst [TiCp(OMe)<sub>3</sub>], signals proving the presence of meso defects were found and used for the calculation of syndiotactic purity, see Table 1. Previously reported syndiotacticity of polystyrenes prepared by this catalyst under similar

Table 1

Results of styrene polymerization catalyzed by studied titanium(IV) alkoxide complexes.

| Run                     | Catalyst   | $10^{-6} \cdot A$<br>[g mol <sup>-2</sup> h <sup>-1</sup> ] | Conversion<br>[%] | Tm <sup>c</sup><br>[°C] | w <sub>c</sub> <sup>c</sup> [%] | SY <sup>d</sup><br>[%] |
|-------------------------|--|---|-------------------|-------------------------|---------------------------------|------------------------|
| <b>1.1</b> <sup>a</sup> | [TiCp(OMe) <sub>3</sub> ]  | 9.31  | 44.8              | 260                     | 51                              | 97.6                   |
| <b>1.2</b> <sup>b</sup> | $[Ti(\eta^5-C_5H_4)SiMe_3)(OMe)_3]$  | 13.75   | 66.1              | 268                     | 53                              | >99                    |
| 1.3 <sup>b</sup>        | $[\text{Ti}(\eta^5 - \text{C}_5\text{H}_4 \text{SiMe}_3)(\text{OPr}^i)_3]$ | 1.31  | 6.3               | 269                     | 49                              | >99                    |
| <b>1.4</b> <sup>b</sup> | $[\text{Ti}(\eta^5 - \text{C}_5\text{H}_4 \text{SiMe}_3)(\text{OBu}^t)_3]$ | 7.45  | 35.8              | 270                     | 43                              | >99                    |
| 1.5 <sup>b</sup>        | 7  | 1.45  | 7.0               | 268                     | 47                              | >99                    |
| 1.6 <sup>b</sup>        | 8  | 0.48  | 2.3               | 267                     | 55                              | _ e                    |
| 1.7 <sup>b</sup>        | 9  | 1.36  | 6.5               | 268                     | 57                              | >99                    |
| 1.8 <sup>b</sup>        | 10   | 1.76  | 8.4               | 270                     | 65                              | >99                    |

 $^a$  Polymerization conditions: [styrene] = 1.45 M, Al/Ti = 500, reaction time 60 min, toluene,  $T_P=50~^\circ\text{C}$ , total volume 12 ml, [Ti] = 417  $\mu\text{M}.$ 

[Ti] = 420 μM.

<sup>c</sup> Melting point ( $T_m$ ) of PS and degree of crystallinity ( $w_c$ ) were determined by DSC from the second heating run.

<sup>d</sup> % of *rrrrrr* heptads according to <sup>13</sup>C NMR.

<sup>e</sup> Not determined due to low yield of PS.

polymerization conditions (SY = 87-93%) are lower probably due to different method used for *s*-PS content determination (extraction in refluxing 2-butanone) [7,42].

# 4. Conclusions

This paper describes the preparation and properties of trimethylcyclopentadienes and half-sandwich titanium(IV) complexes bearing alkoxydimethylsilyl group. The diene C<sub>5</sub>H<sub>4</sub>(SiMe<sub>3</sub>)(Si-Me<sub>2</sub>OMe) reacts with TiCl<sub>4</sub> giving corresponding (methoxy-dimethylsilyl)cyclopentadienyl titanium(IV) trichloride in low yield. This titanium complex is thermodynamically unstable and slowly turns into the mixture of  $[TiCl_3(\eta^5-C_5H_4SiMe_2Cl)]$  and methoxytitanium compounds in both solution and in gaseous phase. Fully alkoxylated complexes of the type  $[Ti(\eta^5-C_5H_4SiMe_2OR)(OR)_3]$ , where R is Me, i-Pr or t-Bu, could be synthesized from chlorosilylcyclopentadienyltitanium(IV) trichlorides by treatment with ROH/NEt<sub>3</sub> or *t*-BuOK. Analogously, the compound  ${Ti[\eta^5-C_5H_4Si-$ Me(OMe)<sub>2</sub>](OMe)<sub>3</sub>} has been prepared and characterized. All alkoxylsilyl-substituted titanium compounds show catalytic behavior in styrene polymerization, but their activity is significantly lower than that observed for corresponding trimethylsilylsubstituted titanium(IV) alkoxides. The lower activity of alkoxysilyl-substituted catalysts could be attributed to possible  $O \rightarrow Al$  interaction with methylaluminoxane that hinders catalytically active site. All prepared polystyrenes showed both high melting point and high degree of syndiotacticity as has been determined by DSC and <sup>13</sup>C NMR spectroscopy, respectively.

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# Appendix A. Supplementary material

CCDC 902807 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/ data\_request/cif.

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