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Synthesis, structure characterization and catalytic activity of lanthanide complexes containing an *ansa* carbonous-bridged cyclopentadienyl – thienyl ligand

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A kind of new lanthanocene complex with an *ansa* carbonous-bridged cyclopentadienyl/aromatic heterocycle ligand was prepared and characterized. Based on the data of elemental analyses, MS and IR, they were presumed to be solvent-free complexes (cyclo-$C_4H_3SCMe_2C_5H_4)_2LnCl$ [Ln=Er (1), Dd (2), Y (3), Sm (4)]. These complexes were effective for the polymerization of methyl methacrylate in the presence of co-catalyst. When $AlEt_3$ and NaH (nanometric) were used as different co-catalysts, the lanthanocene complexes 1–4 showed different catalytic behavior. These differences resulted from the formation of different active species. The catalyst system (cyclo-$C_4H_3SCMe_2C_5H_4)_2LnCl$/NaH (nanometric) showed high catalytic activity (yield ≥95% and $M\eta > 10^5$) in a short time at the ambient temperature.

Keywords: lanthanocene complexes; *ansa* carbonous-bridged cyclopentadienyl-thienyl ligands; nanometric sodium hydride; polymerization of methyl methacrylate

Introduction

Nowadays, lanthanide catalysts are widely employed in the field of coordination polymerization because they can produce high added-value polymers or copolymers.[1–4] Therefore, the development of new ancillary ligands to support catalytic reactivity at lanthanide metal centers is currently an intensively studied area.[5–8] *ansa* Carbonous-bridged cyclopentadienyl ligands have received much attention due to the often dramatic effects on both the stability and the behavior of reactivity and catalytic activity of lanthanocene complexes by the incorporation of the *ansa*-bridge substituent which coordinates with the center metal.[9–15] Usually, alkenyl, phenyl, donor atom (O, N and S) functionalized side chains are used as substituents in lanthanocene. However, few studies have reported on organolanthanide complexes containing the bridged cyclopentadienyl/aromatic heterocycle ligands. The aromatic heterocycle compounds (furan, pyridine or thiophene) as an aromatic system can coordinate to the metal center by η^5, and also the heteratom as a donor may coordinate to metal center by η^1. The bimodal δ/π-coordination capability of these groups may allow for the fine-tuning of the coordination to the lanthanide center in the lanthanide complexes.[16] Therefore we were interested to find out whether *ansa*-bridged aromatic heterocycle-cyclopentadienyl lanthanides complexes display special catalytic activity. Here, we report the synthesis and characterization of bridged thienyl/cyclopentadienyl lanthanocene complexes, and the catalytic activity for polymerization of methyl methacrylate (MMA) is also described.

Experimental

Materials and methods

Synthesis and handling of all air- and moisture-sensitive compounds were manipulated under an inert atmosphere of argon using Schlenk techniques. Toluene and THF were refluxed over sodium and benzophenone and distilled under argon prior to use. The preparation of anhydrous lanthanide trichloride (Ln = Sm, Gd, Dy, Er)[17] and nanometeric sodium hydride,[18] and the purification of MMA were carried out according to published procedures.[13] Elemental analyses for carbon and hydrogen were performed on an EA1106 CHN analyzer. Mass spectra were recorded on an HP 5989A spectrometer. Infrared spectra were obtained on a Nicolet 5SXC spectrometer in the form of KBr pellets. The molecular weight of poly(MMA) in $CHCl_3$ was determined at 30 °C by a Ubbelohde-type viscometer according to $[\eta] = 5.5 \times 10^{-3}\ M\eta^{0.79}$ (cm^3/g) ($M\eta$ = viscosity average molecular weight). Molecular weight distributions were determined using a Waters-208LC/GPC chromatogram using polystyrene columns as a standard. Tacticities of polymers were determined by ^1H NMR spectra (from the peak of α-methyl, *mm*, *mr* and *rr* at δ 1.17, 0.98 and 0.78 respectively).[19] ^1H NMR spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer at room temperature in $CDCl_3$.

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Synthesis of the complexes cylo-$C_4H_3SCMe_2C_5H_4Li$

To a solution of 2-bromothiophene (4.0 g, 0.0245 mol) in petroleum ether (20 ml) was added dropwise *n*-BuLi (13 ml, 1.86 mol/l, 0.0245 mol) in *n*-hexane at −50 °C. During the addition, a white solid was precipitated. After the addition, the mixture was warmed to room temperature and stirred overnight. After filtering, washing with petroleum ether and drying under vacuum, 1.87 g (85%) of 2-thienyl lithium was obtained as a white powder. A solution of 2-thienyl lithium (1.87 g, 0.0208 mol) in diethyl ether was cooled to 0 °C, and 2.20 g (0.0208 mol) 6,6-dimethyl fulvene was added dropwise over 30 min. Then the mixture was warmed to room temperature, stirred for 4 h, hydrolyzed with water and extracted twice with Et_2O. The combined organic phase was dried over $MgSO_4$ and the solvent was removed under vacuum. The residue was distilled under reduced pressure, and 2.0 g (42%) of cyclo-$C_4H_3SCMe_2C_5H_5$ as a colourless liquid was collected at 57–60 °C/1 mmHg.

To a solution of cyclo-$C_4H_3SCMe_2C_5H_5$ (2.0 g, 0.011 mol) in petroleum ether (50 ml), *n*-BuLi (7 ml, 1.57 mol/l, 0.011 mol) in *n*-hexane was added dropwise at −30 °C. The mixture was warmed to room temperature, stirred overnight and a huge amount of white solid was precipitated. After filtering, washing with petroleum ether and drying under vacuum, 1.65 g (76.7%) of cyclo-$C_4H_3SCMe_2C_5H_4Li$ as a white powder was obtained.

Synthesis of the complexes (cyclo-$C_4H_3SCMe_2C_5H_4)_2LnCl$ [Ln = Er (1), Dd (2), Y (3), Sm (4)]

The general synthetic procedure for the complexes (cyclo-C_4H_3S-$CMe_2C_5H_4)_2LnCl$ is similar. Typically, to a suspension of $ErCl_3$ (0.59 g, 2.19 mmol) in THF (40 ml) was added cyclo-$C_4H_3SCMe_2C_5H_4Li$ (0.90 g, 4.57 mmol) at room temperature, and the reaction mixture was stirred for 24 h at 40 °C. The precipitate was separated by centrifugation and the solvent was removed *in vacuo*. The residue was extracted with toluene (30 ml), and the supernatant was concentrated. Pink crystalline solid was precipitated at −15 °C, then, the crude product was recrystallized from toluene to give 0.31 g (24%) of **1** as pink crystals. The complexes were characterized by elemental analyses, MS and IR. Analytical data are presented below:

(cyclo-C_4H_3S-$CMe_2C_5H_4)_2ErCl$ (**1**): pink crystals (yield = 24%). m.p. 130 °C. Anal. calcd for $C_{24}H_{26}ClErS_2$: C, 49.58; H, 4.51. Found: C, 49.53; H, 4.54. MS (70 eV) *m/z* (%): 581 ([M]$^+$, 8), 546 ([M − Cl]$^+$, 1) 392 ([M − ligand]$^+$, 52), 190 ([ligand]$^+$, 49). IR (KBr): 3098(m), 2966(m), 2929(w), 1475(w), 1460(w), 1381(w), 1360(m), 1237(m), 1201(w), 1137(m), 1031(w), 848(m), 833(m), 781(s), 695(s) cm^{-1}.

(cyclo-$C_4H_3SCMe_2C_5H_4)_2DyCl$ (**2**): pale yellow crystals (yield = 29%). m.p. 154 °C. Anal. calcd for $C_{24}H_{26}ClDyS_2$: C, 50.00; H, 4.55. Found: C, 50.02; H, 4.35. MS (70 eV) *m/z* (%): 577 ([M]$^+$, 9), 542 ([M − Cl]$^+$, 2), 388 ([M − ligand]$^+$, 61), 190 ([ligand]$^+$, 57). IR (KBr): 3098(m), 2966(m), 2929(w), 1476(w), 1461(w), 1381(w), 1360(m), 1238(m), 1202(w), 1138(m), 1032(w), 848(m), 832(m), 778(s), 696(s) cm^{-1}.

(cyclo-$C_4H_3SCMe_2C_5H_4)_2YCl$ (**3**): white crystals (yield = 39%). m.p. 146 °C. Anal. calcd for $C_{24}H_{26}ClS_2Y$: C, 57.31; H, 5.21. Found: C, 57.24; H, 5.18. MS (70 eV) *m/z* (%): 502 ([M]$^+$, 13), 467 ([M − Cl]$^+$, 3) 313 ([M − ligand]$^+$, 100), 190 ([ligand]$^+$, 37). IR (KBr): 3098(m), 2967(m), 2929(w), 1475(w), 1462(w), 1382(w), 1361(m), 1237(m), 1201(w), 1139(m), 1033(w), 848(m), 832(m), 779(s), 696(s) cm^{-1}.

(cyclo-$C_4H_3SCMe_2C_5H_4)_2SmCl$ (**4**): yellow crystals (yield = 38%). m.p. 152 °C. Anal. calcd for $C_{24}H_{26}ClS_2Sm$: C, 51.07; H, 4.69. Found: C, 51.04; H, 4.69. MS (70 eV) *m/z* (%): 565 ([M]$^+$, 6), 530 ([M − Cl]$^+$, 5), 376([M − ligand]$^+$, 49), 190 ([ligand]$^+$, 43). IR (KBr): 3085(m), 2966(m), 2929(w), 1476(w), 1461(w), 1381(w), 1361(m), 1255(m), 1238(w), 1138(m), 1032(m), 837(m), 773(s), 695(s) cm^{-1}.

Polymerization of MMA

The corresponding lanthanide complexes (20–40 mg) were dissolved in toluene, activated with co-catalyst ($AlEt_3$, NaH or nanometric NaH or LiH), and then the required amount of MMA was charged. Polymerization was carried out at a constant temperature for a selected period of time, then, quenched by the addition of acidified ethanol (5% HCl). The polymer was washed twice with ethanol and dried to constant weight at 50 °C in a vacuum oven.

Results and Discussion

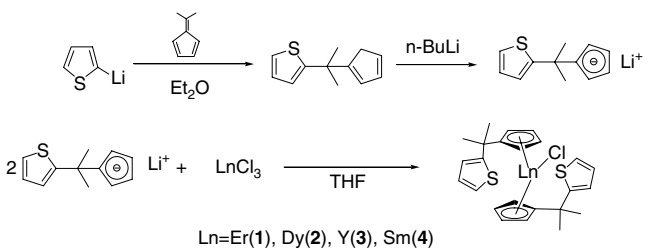
Synthesis and characterization

ansa-Carbonous-bridged thienyl/cyclopentadienyl ligands were obtained with yield of 42% by the reaction of 6,6-dimethyl-fulvene with 2-thienyl lithium in Et_2O at 0 °C.[20] Then the substituted cyclopentadiene was deprotonated with *n*-butyllithium in hexane. The reaction of the substituted cyclopentadienyl anion with $LnCl_3$ (Ln = Sm, Y, Dy, Er) in a 2 : 1 molar ratio in THF at room temperature gave the solvent-free complexes (cyclo-$C_4H_3SCMe_2C_5H_4)_2LnCl$ [Ln = Er (**1**), Dd (**2**), Y (**3**), Sm (**4**)], as shown in Scheme 1. Four complexes are sensitive towards air and moisture and soluble in THF, Et_2O and toluene, but insoluble in hexane (Scheme 1).

All complexes were characterized by elemental analysis, mass spectra and infrared spectra. The IR spectra of all four complexes showed similar patterns and displayed characteristic absorptions of thiophene which was substituted at the 2 position at 3097, 1475, 1460, 1360, 780, 696 cm^{-1}. In the MS spectra of complexes **1–4,** the molecular ion peak was detected, and in combination of the IR and elemental analysis data, the complexes of **1–4** were presumed to be monomeric and solvent-free complexes, and had the general formula (cyclo-C_4H_3S $CMe_2C_5H_4)_2LnCl$.

Polymerization of MMA catalyzed by (cyclo-$C_4H_3SCMe_2C_5H_4)_2LnCl$

The synthesized lanthanocene complexes (**1–4**) were used as catalyst precursors for the polymerization of MMA, and NaH (nanometric) or $AlEt_3$ was use as co-catalyst. NaH (or nanometric NaH) was a good co-catalyst for the polymerization of MMA catalyzed by the lanthanocene complexes in our recent report.[14,15] The results were summarized in Table 1. The results indicated that the lanthanocene complexes **1–4** show catalytic behavior differently with the different co-catalysts. When nanometric sodium hydride was used as the co-catalyst, all of the



Scheme 1. Synthetic route of the lanthanide complexes with a thiophene-pendant cyclopentadienyl ligand.

Table 1. The polymerization of MMA catalyzed by [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2LnCl$ **(1–4)**

Run	Catalyst	Co-catalyst	Cocatalyst/catalyst (molar ratio)	Temperature (°C)	Time (h)	Yield (%)	$M\eta \times 10^{-3}$
1	**1** (Er)	NaH[a]	20	20	1	100	82.2
2	**2** (Dy)	NaH[a]	20	20	1	95	82.5
3	**3** (Y)	NaH[a]	20	20	1	100	115.2
4	**4** (Sm)	NaH[a]	20	20	1	100	118.4
5	**1** (Er)	$AlEt_3$	10	50	20	28	206.1
6	**2** (Dy)	$AlEt_3$	10	50	20	48	252.8
7	**3** (Y)	$AlEt_3$	10	50	20	34	95.8
8	**4** (Sm)	$AlEt_3$	10	50	20	41	93.5

Polymerization conditions: MMA/catalyst (molar ratio) = 800:1; solvent, toluene (2 ml); [a] nanometric.

complexes **1–4** exhibited high catalytic activity: within 1 h, the yield of polymerization was more than 95%, and the molecular weight was more than 0.8×10^5. The activity of complexes **1–4** also increased appreciably with the rise of the center lanthanide ionic radius. For example, the molecular weight of the resultant polymer was largest (1.2×10^6) when the center metal was Sm (Table 1, run 4), but it was 0.8×10^6 when the center metal was Er or Dy (Table 1, runs 1 and 2), whereas, when $AlEt_3$ was used as co-catalyst, the complexes **1–4** showed activity only under the condition of higher temperature with a longer reaction time: the polymer yield was about 28–48% at 50 °C after 20 h. The increasing activity order was approximately opposite the order of the center lanthanide ionic radius: the polymer yield reached 48% and the molecular weight was the largest (2.5×10^6) when the center metal was dysprosium (Table 1, run 6). These differences resulted from the formation of different active species in the catalytic system. According to the reports,[21,22] the reaction of RCp_2LnCl reaction with NaH gave RCp_2LnH, and the organolanthanide hydride showed high catalytic activity for the polymerization of polar monomers or non-polar monmers.[23] In the system [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2LnCl$/NaH (nanometric), the catalytic precursor [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2LnCl$ was reacted with NaH to form [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2LnH$ *in situ*, and the corresponding hydride as active center catalyzed the polymerization of MMA. Furthermore, the activity of the system reached that of organolanthanide hydride ($[SmH(C_5Me_5)_2]_2$: yield = 99%, Mn = 58×10^3).[23] In the system [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2LnCl/AlEt_3$, [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2Ln(\mu\text{-}Et)_2$ $Al(Et)_2$ was formed as an active center, which has been proved by ^1H NMR and X-ray diffraction study in a similar system.[24] In addition, the different trend in influence of the center ionic radius on the catalytic activity supported the hyposthesis that the different active species formed in the catalytic system [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2LnCl$ used different co-catalysts. In the catalytic system [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2LnCl$/NaH, the larger ionic radius was propitious to the coordination of monomer to [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2LnH$ as active species, while in the system [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2LnCl/AlEt_3$, the combination of a sterically bulky ligand with a small metal center is of benefit to form a more unsymmetric η^5 coordination of the five-membered ring as well as to stabilize active centers.[25] This behavior was also observed in polymerization of MMA initiated by $RCp_2Ln\text{-}CH_3$.[26]

The co-catalysts also influenced the microstructure of the polymer. The results are summarized in Table 2. Using [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2SmCl$ (**4**) as the catalytic precursor, as $AlEt_3$ was used as the co-catalyst, the polymer obtained was moderate syndiotactic (rr = 60%; Table 2, run 5), while the polymer was atactic which was obtained in the catalytic system with sodium hydride (nanometric) (Table 2, runs 4, 9 and 10), even with the polymerization temperature decreased to 0 °C (Table 2, run 9). The result also supported that the different active species were formed in the catalytic system [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2LnCl$ using different co-catalysts. However, the molecular weight distributions (M_w/M_n) of polymers obtained from the two different catalytic systems were similar: the molecular weight distribution was narrow ($M_w/M_n \approx 2$) and the GPC curves were unimodal (Table 2, runs 4 and 5).

In the catalytic system[cyclo-$C_4H_3SC(Me)_2C_5H_4]_2SmCl$ (**4**)/NaH (nanometric), the effects of such factors as temperature, time of polymerization and variation of the molar ratio of MMA/Ln and co-catalyst/Ln were studied. The results were presented in Table 3. As the molar ratio of MMA/catalyst increased, the catalytic activity reached the maximum at 800 (molar ratio of MMA/catalyst), then began to decrease (Table 3, runs 4, 11–14). The active species, organolanthanide hydride, may initiate the living polymerization of MMA to give increased molecular weight of the polymer with the increase in monomer concentration.[23] However, the decrease in molecular weight in the system may be responsible for the existence of the excess co-catalyst, quickened chain transfer chain and chain termination of polymerization. For the same molar ratio of MMA/catalyst (800), the molecular weight of obtained polymer showed a trend of decrease with increase in temperature from 0 to 40 °C (Table 3, runs 4, 9 and 15). This suggests that there occur more side reactions such as transesterifications under the higher temperature during the polymerization, and the yield and the molecular weight of the resultant polymer increased as time increased.

Table 2. Influence of co-catalyst on the microstructure of the polymer obtained in [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2SmCl$ (**4**) catalytic system

Run	Co-catalyst	Co-catayst/catalyst (molar ratio)	Temperature (°C)	Time (h)	Yield (%)	M_w/M_n	$M_n \times 10^{-3}$	Tacticity *mm* (%)	Tacticity *mr* (%)	Tacticity *rr* (%)
4	NaH[a]	20	20	1	100	2.3	118.4	36	46	18
5	$Al(Et)_3$	10	50	20	41	2.1	93.5	6	34	60
9	NaH[a]	20	0	1	36	–	122.3	33	46	21
10	NaH[a]	10	20	1	92	–	126.4	29	51	20

Conditions: MMA/catalyst (molar ratio) = 800:1, solvent : toluene; [a] nanometric NaH.

Table 3. Polymerization of MMA catalyzed by [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2SmCl$ (**4**)/NaH (nanometric) system

Run	MMA/catalyst (molar ratio)	Cocatalyst/catalyst (molar ratio)	Temperature (°C)	Time	Yield (%)	$M\eta \times 10^{-3}$
4	800	20[a]	20	1 h	100	118.4
11	400	20[a]	20	1 h	100	80.5
12	1200	20[a]	20	1 h	66	94.6
13	1600	20[a]	20	1 h	59	78.5
14	2000	20[a]	20	1 h	17	72.4
9	800	20[a]	0	1 h	36	122.3
15	800	20[a]	40	1 h	82	50.8
16	800	20[a]	20	15 min	80	43.3
17	800	20[a]	20	30 min	99.5	71.2
18	800	20[a]	20	2 h	100	94.8
10	800	10[a]	20	1 h	92	126.4
19	800	40[a]	20	1 h	89	75.6
20	800	20[b]	20	1 h	24	64.6

Co-catalyst: [a] NaH (nanometric); [b] LiH (nanometric).

The catalytic system [cyclo-$C_4H_3SC(Me)_2C_5H_4]_2SmCl$ (**4**)/NaH showed high activity (yield = 92%, $M_n = 126.4 \times 10^3$) at the molar ratio of nanometric NaH/Ln of 10 (Table 3, run 10). As the molar ratio of nanometric NaH/Ln increased, the yield of polymerization increased, but the molecular weight of the polymer decreased due to the fact that the chain transfer of polymerization was quickened by the increase of the concentration of NaH (nanometric) (Table 3, runs 4, 10 and 18). When nanometric LiH was used as co-catalyst, the activity of the catalytic system decreased (Table 3, run 20).

Conclusion

Four novel *ansa* carbonous-bridged thiophene/cyclopentadienyl lanthanocene complexes were synthesized. They were characterized by elemental analysis, mass spectra and infrared spectroscopy. The synthesized complexes showed good catalytic activity for the polymerization of MMA. The catalytic system using the different co-catalysts ($AlEt_3$ or nanometric NaH) had different active species. The different active species resulted from the different catalytic activity and the different microstructure of the polymer. When the nanometric NaH was used as the co-catalyst, the complexes were highly effective for the polymerization of MMA at the ambient temperature.

References

[1] P. M. Zeimentz, S. Arndt, B. R. Elvidge, J. Okuda, *Chem. Rev.* **2006**, *106*, 2404.
[2] H. Yasuda, *J. Polym. Sci. Polym. Chem. Edn* **2001**, *39*, 1955.
[3] Z. Hou, Y. Wakatsuki, *Coord. Chem. Rev.* **2002**, *231*, 1.
[4] S. Arndt, J. Okuda, *Chem. Rev.* **2002**, *102*, 1953.
[5] S. Wang, X. Tang, A. Vega, J. Saillard, S. Zhou, G. Yang, W. Yao, Y. Wei, *Organometallics* **2007**, *26*, 1512.
[6] C. Cui, A. Shafir, C. L. Reeder, J. Arnold, *Organometallics* **2003**, *22*, 3357.
[7] Z. Xie, *Acc. Chem. Rev.* **2003**, *36*, 1.
[8] P. L. Arnold, S. Liddle, *Chem. Commun.* **2005**, 5638.
[9] C. Qian, W. Nie, J. Sun, *J. Organomet. Chem.* **2001**, *626*, 171.
[10] C. Qian, W. Nie, Y. Chen, J. Sun, *J. Organomet. Chem.* **2002**, *645*, 82.
[11] W. Nie, C. Qian, Y. Chen, J. Sun, *J. Organomet. Chem.* **2002**, *647*, 114.
[12] J. Cheng, D. Cui, W. Chen, T. Tang, B. Huang, *J. Organomet. Chem.* **2002**, *658*, 153.
[13] Y. Qian, M. D. Bala, M. Yousaf, H. Zhang, J. Huang, J. Sun, C. Liang, *J. Mol. Cat. A, Chem.* **2002**, *188*, 1.
[14] X. Xie, J. Huang, *Appl. Organometal. Chem.* **2004**, *18*, 282.
[15] X. Xie, J. Huang, *Chin. J. Chem.* **2005**, *23*, 85.
[16] M. Ganesan, C. D. Bérubé, S. Gambarotta, G. P. A. Yap, *Organometallics* **2002**, *21*, 1707.
[17] M. D. Joylor, C. P. Carter, *J. Inorg. Nucl. Chem.* **1962**, *24*, 387.
[18] Y. Zhang, S. Liao, X. Yun, *J. Mol. Cat. A, Chem.* **1993**, *84*, 211.
[19] R. C. Fergeson, D. W. Ovenall, *Polym. Prep.* **1985**, *26*, 182.
[20] J. Huang, T. Wu, Y. Qian, *Chem. Commun.* **2003**, 2816.
[21] K. Qian, R. D. Fisher, G. J. Paolucci, *J. Organomet. Chem.* **1993**, *456*, 185.
[22] C. Qian, Y. Ge, D. Deng, Y. Gu, C. Zhang, *J. Organomet. Chem.* **1988**, *344*, 175.
[23] H. Yasuda, H. Yamamoto, M. Yamashita, K. Yokota, A. Nakamura, S. Miyake, Y. Kai, N. Kanehisa, *Macromolecules* **1993**, *26*, 7134.
[24] M. G. Klimpel, J. Eppinger, P. Sirsch, W. Scherer, R. Anwander, *Organometallics* **2002**, *21*, 4021.
[25] H. Sun, S. Chen, Y. Yao, Q. Shen, K. Yu, *Appl. Organometal. Chem.* **2006**, *20*, 310.
[26] H. Yasuda, H. Yamamoto, M. Yamashita, K. Yokota, A. Nakamura, S. Miyake, Y. Kai, N. Kanehisa, *Macromolecules* **1993**, *26*, 7134.