Available online at www.sciencedirect.com
SCIENCE DIRECT®

Catalysis Today 93–95 (2004) 281–285

CATALYSIS TODAY
www.elsevier.com/locate/cattod

Effect of substituent position on the ethylene polymerization by Fe(II) and Co(II) pyridyl bis-imine catalysts

Il Kim*, Byeong Heui Han, Yun-Seon Ha, Chang-Sik Ha, Dae-Won Park

Division of Chemical Engineering, Pusan National University, Busan 609-735, Republic of Korea

Abstract

Polymerizations and oligomerizations of ethylene by using a series of bis(imino)pyridyl Co(II) and Fe(II) complexes {[(2-ArN=C(Me))$_2$C$_5$H$_3$N]MCl$_2$} (Ar = 2,6-C$_6$H$_3$Me$_2$, **1**; 2,5-C$_6$H$_3$Me$_2$, **2**; 2,4-C$_6$H$_3$Me$_2$, **3**; 2,3-C$_6$H$_3$Me$_2$, **4**; M=Co, **a**; Fe, **b**) bearing two methyl substituents on each imine aryl group are reported. These complexes, when activated with methylaluminoxane in aromatic or aliphatic hydrocarbon solvents, oligomerize or polymerize ethylene to α-olefins or high polymers with exceptionally high activities and selectivities. The activities and selectivities to α-olefins or high polymers are dependent on the catalyst structure and the type of metal. The steric bulk around the metal center is key to retarding chain transfer to obtain high molecular weight polyethylene.

Keywords: Late transition metal chemistry; Iron and cobalt; Pyridyl bis-imine ligands; Ethylene polymerization

1. Introduction

Ethylene polymerization and oligomerization processes catalyzed by transition metal have become of great importance in both academic and industrial fields. In the past late transition metal catalysts were generally accepted that they produced oligomers because of the accelerated β-hydride elimination [1]. An industrial process, SHOP (shell higher olefin process), is an example to produce oligomers by using homogeneous chelate Ni(II) complexes [2-5]. However, in 1995 Brookhart and coworkers succeeded in polymerizing ethylene to high polymers by using Ni, Pd catalysts [2]. And in 1998, a new series of Fe(II) and Co(II) complexes with bis(imino)pyridyl ligands were reported by Gibson and coworkers [6], Bennett from Dupont [7] and Brookhart and coworkers [8], which showed exceptionally high activity for the ethylene polymerization. The melting points of produced polyethylene by these catalysts appeared at 133–139 °C. Especially in contrast to the nickel and palladium systems, there was no chain walking and the polyethylene was strictly linear with very high density [2,9]. They reported that the key to high polymer production was the incorporation on the aryl rings of bulk *ortho* substituents that greatly retarded the rate of chain transfer [6,8]. Also, Brookhart group reported that by reducing the steric bulk of these pyridyl bisimine ligands the resultant iron catalysts oligomerized ethylene to linear α-olefins with remarkably high activity and selectivity while maintaining desirable oligomer distributions [10]. Here we report how the polymerization behaviors of iron and cobalt complexes prepared by changing the position of two methyl substituents on the aryl ring (Scheme 1) are changed according to the substituents position and the type of metal.

2. Experimental

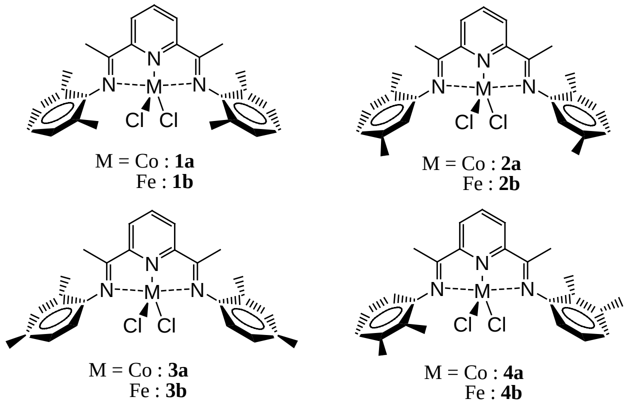
2.1. Materials

All reactions were performed under a purified nitrogen atmosphere using standard glove box and schlenk technique. Polymerization grade of ethylene (SK Co., Korea) was purified by passing it through columns of Fisher RIDOX^{TM} catalyst and molecular sieve 5 Å/13X. Organic solvents were distilled from Na/benzophenone and stored over molecular sieves (4 Å). All reagents used in this study were purchased from Aldrich Chemical Co. and used without further purification. Methylaluminoxane (MAO, 8.4 wt.% total Al solution in toluene) purchased from Akzo Chemical was used without further purification.

---

* Corresponding author. Tel.: +82 51 510 2466; fax: +82 51 513 7720.
E-mail address: ilkim@pnu.edu (I. Kim).

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.06.057



M = Co : **1a**
Fe : **1b**

M = Co : **2a**
Fe : **2b**

M = Co : **3a**
Fe : **3b**

M = Co : **4a**
Fe : **4b**

Scheme 1. A series of bis(imino)pyridyl cobalt and iron complexes utilized in this study.

2.2. *Syntheses of metal complexes and polymerization of ethylene*

Literature procedures [8] were employed to synthesize homogeneous **1a** and **1b** complexes. The other cobalt and iron complexes (**2**–**4**) were prepared by the similar procedures. As an example, 2,6-bis-[2-2,5-dimethylphenylimino]ethyl] pyridine ligand was prepared as follows. 2,6-Diacetylpyridine (990 mg, 6.1 mmol) and 2,6-dimethylaniline (excess) were dissolved in 30 mL of CH_3OH in a round-bottom flask. Five drops of formic acid were added, and the sealed solution mixture was stirred at 50 °C overnight. The solution was cooled in an ice bath, resulting in the formation of a light yellow precipitate that was isolated by filtration. ^1H NMR ($CDCl_3$) δ 8.29 (d, 2, Py–Hm), δ 7.80 (t, 1, Py–Hp), δ 7.14 (d, 4, Ar–Hm), δ 6.99 (t, 2, Ar–Hp), δ 2.23 (s, 6, N=CMe), δ 2.19 (s, 6, Ar–Me), δ 1.96 (s, 6, Ar–Me).

For the synthesis of the metal complexes, the ligand (1.1 equiv.) and the metal salt ($CoCl_2$ or $FeCl_2$) were added together in a schlenk flask under nitrogen. Stirring was begun and continued for 4 h. Diethylether was added to the reaction to precipitate the complex, and the resultant solids were filtered in air and washed with Et_2O and pentane and dried in vacuo. In this way $[(2\text{-}(2,5\text{-}C_6H_3Me_2)N{=}C(Me))_2C_5H_3N]CoCl_2$ (**2a**, green powder) and $[(2\text{-}(2,5\text{-}C_6H_3Me_2)N{=}C(Me))_2C_5H_3N]FeCl_2$ (**2b**, blue powder) could be isolated as high yields over 90%.

Ethylene polymerization was performed in a 250 mL round-bottom flask equipped with a magnetic stirrer and a thermometer. Detailed polymerization procedures are described elsewhere [11].

2.3. *Characterization*

Thermal analysis of polymer obtained by **1** catalyst was carried out by using differential scanning calorimeter (Perkin-Elmer DSC, model: Pyris 1) at 10 °C/min heating rate under nitrogen atmosphere. The intrinsic viscosity was measured in decalin. At 135 °C using an modified Ubbhelode viscometer and the average of molecular weight was calculated by following equation [12].

$$[\eta] = 6.2 \times 10^{-4}\, M_v^{0.7}$$

Analysis of α-olefins obtained by **2**–**4** catalysts was performed by gas chromatography (HP-6890), which was performed using a J&W Scientific DB608 column (30 m × 0.53 mm) with a FID detector. The injector and detector temperature was kept constant at 250 °C. The temperature program for the GC column was as follows: initial temperature 45 °C, 0 min; ramp 5 °C/min; final temperature 180 °C, 0 min.

3. Results and discussion

Semi-batch polymerizations of ethylene by using Co(II) and Fe(II) complexes (**1**–**4**) were carried out in 80 mL of toluene at 25 °C in the presence of MAO by injecting a prescribed amount of catalyst. Figs. 1 and 2 show polymerization rate (R_p) profiles obtained by Co(II) and Fe(II) complexes. All catalysts showed exceptionally high activities regardless of the catalyst structure. The fast decays of R_p of **2a**, **3a** and **4a** catalysts (Fig. 1) after reaching maximum rate in a minute are due to vapor pressures of α-olefins (especially 1-butene) formed during reaction (*vide infra*). Since the polymerizations were carried out at constant pressure (1.3 bar), accumulation of lower α-olefins such as 1-butene in the semi-batch reactor blocks introduction of ethylene monomer. However, polymerization by **1a** catalyst kept high activity for a period of polymerization (30 min), since this catalyst gives high polymers (*vide infra*).

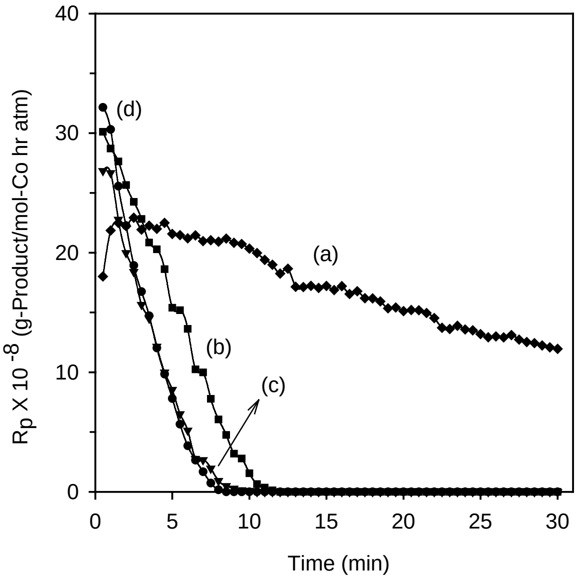


Fig. 1. R_p vs. time of ethylene polymerization and oligomerization catalyzed by (a) **1a**/MAO, (b) **2a**/MAO, (c) **3a**/MAO, (d) **4a**/MAO with [Co] = 6.04 μmol, 80 mL of toluene, $P_{C_2H_4} = 1.3$ bar, $T_p = 30$ °C and [Al]/[Co] = 700.

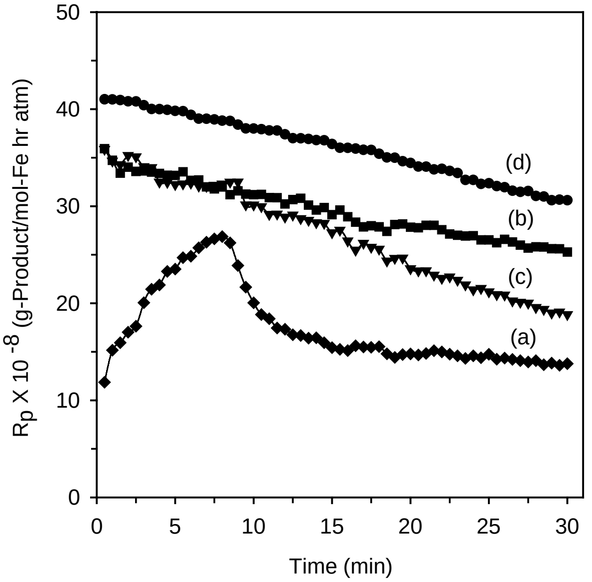


Fig. 2. R_p vs. time of ethylene polymerization and oligomerization catalyzed by (a) **1b**/MAO, (b) **2b**/MAO, (c) **3b**/MAO, (d) **4b**/MAO with [Fe] = 6.04 μmol, 80 mL of toluene, $P_{C_2H_4} = 1.3$ bar, $T_p = 30\,^{\circ}$C and [Al]/[Co] = 700.

All Fe(II) catalysts also showed exceptionally high activities that sustained for 30 min. The **2a**, **3a** and **4a** catalysts give a mixture of α-olefins consisting of 1-butene, 1-hexene, 1-octene and 1-decene. Vapor pressures of these mixtures are negligible at a polymerization temperature (T_p) of 30 °C, resulting in constant activities for a long time. It is interesting to note that the **1a** catalyst yielded high polymer ($M_v = 18,400$). Table 1 summarizes the results of GC analysis of products obtained by Co(II) and Fe(II) catalysts. Cobalt catalysts (**2a**, **3a** and **4a**) not bearing dimethyl substituents at 2- and 6-positions on each aryl ring selectively yield 1-butene as main products. Especially 2,4-dimethyl substituted aryl ring yield 1-butene selectively. For example, the $[(2\text{-}(2,4\text{-}C_6H_3Me_2)N{=}C(Me))_2C_5H_3N]CoCl_2$ complex, which will give the least steric hindrance to the active sites, yields 1-butene as a 91.17% selectivity. However, the selectivity of iron catalysts (**2b**, **3b** and **4b**) to give a specific α-olefin is not so high as corresponding cobalt catalysts. As shown in Table 1, these catalysts result in mixtures of 1-butene, 1-hexene, 1-octene, and a small amount of 1-decene. These results demonstrate that steric bulk around the active metal centers is key to retarding chain transfer in order to obtain high molecular weight polymer. Reduction of ligand bulk by changing position of the methyl substituent on the imine aryl ring causes a selective formation of α-olefins. In general the iron catalysts produce higher molecular weight products than their cobalt analogues.

In order to investigate detailed polymerization behavior of the cobalt and iron catalysts (**1a** and **1b**), polymerizations were carried out at various temperatures between 10 and 70 °C, and at various MAO concentrations. The results are summarized in Table 2. The **1a** and **1b** catalysts show very high activity in a wide range of temperature, even if the activity decreases remarkably when $T_p > 50$. These results demonstrate that the active sites are not so stable at high temperature. The molecular weight of the polyethylene was decreased monotonously with increasing T_p for both catalysts. In all cases **1b** catalyst yields polymers of higher molecular weight than **1a** catalyst at the same polymerization conditions. All catalysts show high activities at low MAO concentrations (say [Al]/[M] = 100). The [Al]/[M] ratio of several hundred is seemed to be enough to achieve maximum activity. This dependence of the [Al]/[M] ration on the activity of the late transition metal catalysts is quite different from that of the metallocene catalysts, in that much higher MAO concentration is need to get maximum activity with the metallocene catalysts. As the MAO concentration increases, the molecular weight of polymer decreases due to the activated transfer reaction to MAO. All polymers obtained by **1a** and **1b** catalysts showed sharp single melting peaks and very high crystallinities, demonstrating they are highly linear. In general polymers obtained by **1b** catalyst show higher melting points than those by **1a** catalyst due to a difference in the molecular weight.

Kinetics of ethylene polymerization to yield α-olefins was investigated by using **2a** catalyst. Reactions were carried out for 10 min by changing the amount of catalyst (2.01 to 18.1 μmol), [Al]/[Co] ratio (100–900), polymerization temperature (10–60 °C), and solvent used (toluene, hexane, and methylene chloride). The results of polymerization are

Table 1
Results of ethylene polymerization and oligomerization by a series of pyridyl bis-imine Co(II) and Fe(II) complexes[a]

Entry	Catalyst	$R_{p,avg}$[b] × 10^{-8} (g PE/mol M h bar)	1-butene (%)	1-hexene (%)	1-octene (%)	1-decene (%)
1	**1a**	15.6590	Gives polyethylene (see Table 2)			
2	**2a**	5.1780	87.41	10.85	1.34	0.4
3	**3a**	3.2744	91.17	6.83	0.81	1.19
4	**4a**	3.4173	83.78	9.58	2.67	3.97
5	**1b**	20.3878	Gives polyethylene (see Table 2)			
6	**2b**	29.5929	28.75	36.08	33.62	1.55
7	**3b**	27.0358	25.33	32.54	34.08	8.05
8	**4b**	36.0695	24.57	31.9	36.31	7.22

[a] Polymerization conditions: [MAO]/[M] = 700, 80 mL of toluene, $T_p = 30\,^{\circ}$C, $P_{C_2H_4} = 1.3$ bar and 6.04 μmol of catalyst.

[b] Average rate of polymerization (or oligomerization) for a period of reaction.

Table 2
Results of ethylene polymerization by $[(2\text{-}(2,6\text{-}C_6H_3Me_2)N{=}C(Me))_2C_5H_3N]MCl_2$ (M=Co, Fe) in the presence of MAO[a]

Entry	Catalyst	T_p (°C)	[Al]/[M]	$R_{p,avg}$[b] × 10^{-8} (g PE/mol M h bar)	M_v[c] × 10^{-3}	T_m[d] (°C)	ΔH_f[d] (J/g)	X_c[e] (%)
1	**1a**	30	50	3.2941	6.1	119.1	236.8	88
2	**1a**	30	100	9.1851	6.1	–	–	–
3	**1a**	30	300	13.3609	5.6	116.6	138.3	88
4	**1a**	30	500	17.2977	4.2	–	–	–
5	**1a**	30	700	15.6590	2.4	114.8	228.6	85
6	**1a**	30	1000	15.7049	2.3	–	–	–
7	**1a**	30	3000	8.6112	2.3	112.0	236.0	87
8	**1a**	10	700	15.8871	4.5	118.5	221.7	82
9	**1a**	20	700	16.2993	3.8	118.1	242.5	90
10	**1a**	50	700	5.4588	2.2	107.6	240.2	89
11	**1a**	70	700	0.4554	–	–	–	–
12	**1b**	30	50	2.7911	75.6	130.4	203.0	75
13	**1b**	30	100	15.9709	58.0	–	–	–
14	**1b**	30	300	16.7676	27.3	128.9	206.6	77
15	**1b**	30	500	17.5361	21.4	–	–	–
16	**1b**	30	700	20.3878	18.4	126.4	195.7	73
17	**1b**	30	1000	21.4879	12.6	–	–	–
18	**1b**	30	2000	25.6185	12.3	–	–	–
19	**1b**	30	3000	27.4224	12.3	–	–	–
20	**1b**	10	700	16.3734	36.7	127.6	190.8	71
21	**1b**	20	700	20.2417	22.0	127.2	185.5	69
22	**1b**	50	700	25.1057	17.9	127.3	197.7	73
23	**1b**	70	700	3.3297	14.6	125.5	–	66

[a] Polymerization conditions: run time = 30 min, 80 mL of toluene, $T_p = 30\,^\circ C$, $P_{C_2H_4} = 1.3$ bar and 6.04 μmol of catalyst.
[b] Average rate of polymerization for a period of reaction.
[c] Viscosity average molecular weights calculated from the equation.
[d] Melting temperature (T_m) and heat of fusion (ΔH_f) of the polymer determined by DSC.
[e] Crystallinity calculated by $(\Delta H_f/\Delta H_f^\circ) \times 100$ ($\Delta H_f^\circ = 269.9$ J/g for folded-chain polyethylene) [12].

summarized in Table 3. In general the **2a** catalyst selectively gives 1-butene at all polymerization conditions. Selectivity to yield 1-butene increases as the catalyst concentration decreases, as the [Al]/[Co] ratio increases, and as the T_p increases. As the [Al]/[Co] ratio and T_p increase, the transfer reaction should be activated as expected. The polymerization rate decreases monotonously as the T_p increases from 10 to 60 °C, indicating the active sites are not thermally stable. Only a small amount of MAO (say [Al]/[Co] = 100) is enough to achieve a high polymerization rate. It is very interesting to note that the selectivity to yield 1-butene reaches almost 100%, when nonpolar

Table 3
Results of ethylene oligomerization by $[(2\text{-}(2,5\text{-}C_6H_3Me_2)N{=}C(Me))_2C_5H_3N]CoCl_2$ (**2a**) in the presence of MAO[a]

Entry	Catalyst loading (μmol)	T_p (°C)	Solvent	[Al]/[Co]	$R_{p,avg}$[b] × 10^{-8} (g PE/mol Co h bar)	1-butene (%)	1-hexene (%)	1-octene (%)	1-decene (%)
1	2.01	30	Toluene	500	21.4306	92.70	6.52	0.39	0.39
2	6.04	30	Toluene	500	75.3220	87.41	10.85	1.34	0.40
3	18.1	30	Toluene	500	9.9922	85.21	13.08	1.29	0.42
4	2.01	30	Toluene	100	17.4066	87.93	10.38	1.03	0.66
5	2.01	30	Toluene	300	19.2581	89.96	8.68	0.78	0.58
6	2.01	30	Toluene	700	17.9362	88.28	10.14	0.99	0.59
7	2.01	30	Toluene	900	17.7964	91.33	3.79	1.67	3.20
8	2.01	10	Toluene	500	24.6806	79.74	17.31	2.49	0.45
9	2.01	40	Toluene	500	6.9994	90.39	7.55	1.17	0.88
10	2.01	60	Toluene	500	1.6023	91.33	3.79	1.67	3.20
11	2.01	30	*n*-hexane	500	1.2359	100	–	–	–
12	2.01	30	CH_2Cl_2	500	1.5039	100	–	–	–

[a] Reaction conditions: run time = 10 min, solvent = 80 mL, and $P_{C_2H_4} = 1.3$ bar.
[b] Average rate of polymerization for the period of polymerization.

n-hexane and polar methylene chloride are utilized as solvents, even if the polymerization rates decrease comparing to the case of toluene solvent. These results demonstrate that *n*-hexane and methylene chloride solvents, resulting in low activity and high transfer rates, do not so effectively stabilize the cationic active sites formed during the reaction. Even though the results of polymerization by other catalysts such as **2b**, **3** and **4** are not shown here, selectivity to give a specific α-olefin and activity might be tuned by controlling the catalyst structure, metal type, and polymerization parameter.

4. Conclusions

This paper described the polymerization of ethylene by using a series of pyridyl bis-imine complexes of cobalt and iron. The precatalysts employed were $\{[(2\text{-ArN=C(Me)})_2C_5H_3N]MCl_2\}$ (Ar = 2,6-$C_6H_3Me_2$, **1**; 2,5-$C_6H_3Me_2$, **2**; 2,4-$C_6H_3Me_2$, **3**; 2,3-$C_6H_3Me_2$, **4**; M=Co, **a**; Fe, **b**). In the presence of ethylene and MAO cocatalyst, these complexes exhibit very high activities for the ethylene polymerization and oligomerization. The protective bulk of the *ortho* substituents above and below the metal active centers was critical to the molecular weight of the resulting ethylene polymerizations. As a result only **1a** and **1b** yielded high polymers with very high activities, all other catalysts (**2–4**) selectively yielded α-olefins. In general, the iron catalyst produced higher molecular weight polyethylene than its cobalt analogue. Especially cobalt catalyst (**2a**, **3a** and **4a**) yielded predominantly 1-butene at various polymerization conditions, while corresponding iron catalysts (**2b**, **3b** and **4b**) produced 1-butene, 1-hexene, and 1-octene in a similar amount. All these catalysts were exceptionally active. The selectivity to yield a specific α-olefin and high molecular weight polyethylene might thus be tuned by controlling steric bulk around the metal center, metal type and polymerization parameters.

Acknowledgements

This work was supported by Grant No. R01-2003-000-10020-0 from the Basic Research Program of the Korea Science & Engineering Foundation. IK is also grateful to the Brain Korea 21 Project in 2003.

References

[1] A.A. Montagna, R.M. Burkhart, A.H. Dkmezian, Chemtech 27 (1997) 26.

[2] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169, and reference cited therein.

[3] W. Keim, A. Behr, M. Röper, Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, p. 371.

[4] P.W. Joll, G. Wilkinson, F.G.A. Stone, Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, p. 613.

[5] (a) W. Keim, Chimia 35 (1981) 344;
(b) W. Keim, Fundamental Research in Homogeneous Catalysis, Plenum Press, New York, vol. 4, 1984, p. 131;
(c) W. Keim, Catalytic Transition Metal Hydride, Annals of the New York Academy of Science, vol. 415, 1983, p. 191;
(d) W. Keim, A. Behr, B. Limbäcker, C. Krüger, Angew. Chem. Int. Ed. 20 (1981) 116;
(e) W. Keim, R. Appel, A. Storeck, C. Krüger, R. Goddard, Angew. Chem. Int. Ed. 22 (1983) 503;
(f) M. Peuckert, W. Keim, Organometallics 2 (1983) 594;
(g) W. Keim, Angew. Chem. Int. Ed. Engl. 117 (1995) 1137;
(h) K. Hirose, W. Kiem, J. Mol. Cat. 73 (1992) 271;
(i) W. Kiem, Angew. Chem. Int. Ed. Engl. 29 (1990) 235.

[6] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 849.

[7] A.M.A. Bennett, World Patent Application 98/27124, 1998.

[8] B.L. Small, M. Brookhart, A.M.A. Bennet, J. Am. Chem. Soc. 120 (1998) 4049.

[9] G.J.P. Britovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Masroianni, S.J. McTavish, C. Redshaw, G.A. Solan, S. Stromberg, A.J.P. White, D.J. Williane, J. Am. Chem. Soc. 121 (1999) 8728.

[10] B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143.

[11] I. Kim, B.H. Han, J.G. Kim, H.S. Suh, S.-S. Ha, Macromolecules 36 (2003) 6689.

[12] R. Chang, J. Polym. Sci. 8 (1957) 35.