

Single-Site Catalyst Immobilization Using Magnesium Chloride Supports¹

J. C. Chadwick and J. R. Severn

Dutch Polymer Institute (DPI)/Laboratory of Polymer Chemistry, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands
e-mail: j.c.chadwick@polymers.nl

Received July 11, 2005

Abstract—Immobilization and activation of a broad range of titanium-, chromium- and nickel-based single-site catalysts for ethylene polymerization has been carried out using supports of type $MgCl_2/AlR_n(OEt)_{3-n}$, prepared by reaction of AlR_3 with adducts of magnesium chloride and ethanol. The spherical particle morphology of the support is retained and replicated during catalyst immobilization and polymerization, yielding polyethylenes with controlled particle size and morphology. The single-site nature of these catalysts is also retained, giving polymers with narrow molecular weight distribution. Furthermore, very high catalyst activities can be obtained as a result of a stabilizing effect of the support, which prevents the rapid decay in activity often observed in homogeneous polymerization with these catalysts.

DOI: 10.1134/S0023158406020054

INTRODUCTION

In recent years, considerable research efforts have been applied to the development of effective techniques for the immobilization of homogeneous, single-site catalysts for olefin polymerization, an essential prerequisite for the widespread implementation of such catalysts in polyolefins production [1]. The most commonly used support for the immobilization of a single-site catalyst is silica, but several groups have investigated the use of magnesium chloride, either as support or as (co)activator for a single-site catalyst. Marks [2] showed that $(C_5Me_5)_2ThMe_2$ can be activated by $MgCl_2$, the Lewis acidity of the latter leading to abstraction of a methide anion and generation of a catalytically active center. Soga and Kaminaka [3, 4] used $MgCl_2$ in combination with a zirconocene catalyst and AlR_3 , while Kissin et al. [5] used mixtures of MgR_2 and AlR_2Cl (generating $MgCl_2$ and AlR_3) as cocatalyst components for olefin polymerization using various metallocenes. An important feature of magnesium chloride-based supports for single-site catalysts, which will be highlighted in the present contribution, is the stabilization of the active species. Sivaram [6] found stable kinetics in ethylene polymerization after immobilizing Cp_2TiCl_2 on a $MgCl_2$ -based support, in contrast to the rapid decay normally observed with such metallocenes under homogeneous polymerization conditions.

A particularly useful approach for the preparation of magnesium chloride-based supports that are not only effective for single-site catalyst immobilization and

activation but can also provide excellent control over the particle morphology of the resulting polymer involves the use of $MgCl_2$ /alcohol adducts. Spherical supports of type $MgCl_2 \cdot nEtOH$ are well established as starting materials in Ziegler–Natta catalyst production [7]. Some years ago, it was demonstrated that effective single-site catalyst immobilization of a metallocene could be achieved by partial dealcoholation of an adduct $MgCl_2 \cdot 3EtOH$, followed by reaction with AlR_3 and subsequently with a metallocene [8]. Subsequently, other groups employed similar approaches for the immobilization of methylaluminoxane (MAO) and/or a metallocene [9–11].

Another recent approach to the use of $MgCl_2$ /alcohol adducts in catalyst immobilization and activation comprises the reaction of $Al(i-Bu)_3$ with a hydrocarbon solution of a $MgCl_2$ /2-ethylhexanol adduct, leading to the precipitation of a $MgCl_2/Al(i-Bu)_n(OR)_3-n$ support. These supports proved to be very effective for the activation of Ti-, Zr- and V-based FI catalysts, giving well-defined polymer particle morphology and activities comparable with those obtained via activation with MAO [12, 13].

In the present work, we have investigated the use of supports of type $MgCl_2/AlR_n(OEt)_{3-n}$ obtained by reaction of $AlEt_3$ or $Al(i-Bu)_3$ with adducts of magnesium chloride and ethanol, for the immobilization and activation of a wide range of single-site catalysts, without the use of MAO or a borate activator in polymerization.

¹ The text was submitted by the authors in English.

Table 1. Composition of $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ supports

Starting material	Al alkyl	Product		Composition
		Al, wt %	OEt, wt %	
$\text{MgCl}_2 \cdot 1.1\text{EtOH}$	AlEt_3	4.1	4.9	$\text{MgCl}_2 \cdot 0.18\text{AlEt}_{2,3}(\text{OEt})_{0.7}$
$\text{MgCl}_2 \cdot 1.1\text{EtOH}$	$\text{Al}(i\text{-Bu})_3$	2.8	3.1	$\text{MgCl}_2 \cdot 0.12\text{Al}(i\text{-Bu})_{2,3}(\text{OEt})_{0.7}$
$\text{MgCl}_2 \cdot 2.1\text{EtOH}$	AlEt_3	4.8	5.6	$\text{MgCl}_2 \cdot 0.22\text{AlEt}_{2,3}(\text{OEt})_{0.7}$
$\text{MgCl}_2 \cdot 2.1\text{EtOH}$	$\text{Al}(i\text{-Bu})_3$	2.9	3.8	$\text{MgCl}_2 \cdot 0.13\text{Al}(i\text{-Bu})_{2,3}(\text{OEt})_{0.7}$
$\text{MgCl}_2 \cdot 2.8\text{EtOH}$	AlEt_3	6.0	6.5	$\text{MgCl}_2 \cdot 0.29\text{AlEt}_{2,4}(\text{OEt})_{0.6}$
$\text{MgCl}_2 \cdot 2.8\text{EtOH}$	$\text{Al}(i\text{-Bu})_3$	4.1	4.6	$\text{MgCl}_2 \cdot 0.21\text{Al}(i\text{-Bu})_{2,3}(\text{OEt})_{0.7}$

Table 2. Ethylene polymerization with Cp_2TiCl_2 and related immobilized catalysts

Catalyst	Support	Activity, $\text{kg mol}^{-1} \text{bar}^{-1} \text{h}^{-1}$	\bar{M}_w	\bar{M}_w/\bar{M}_n
Cp_2TiCl_2	$\text{MgCl}_2 \cdot 0.18\text{AlEt}_{2,3}(\text{OEt})_{0.7}$	218	1182000	2.6
Cp_2TiCl_2	$\text{MgCl}_2 \cdot 0.12\text{Al}(i\text{-Bu})_{2,3}(\text{OEt})_{0.7}$	207	729000	2.5
Cp_2TiCl_2	$\text{MgCl}_2 \cdot 0.22\text{AlEt}_{2,3}(\text{OEt})_{0.7}$	327	1106000	2.7
Cp_2TiCl_2	$\text{MgCl}_2 \cdot 0.13\text{Al}(i\text{-Bu})_{2,2}(\text{OEt})_{0.8}$	268	1040000	2.0
$\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N}-t\text{-Bu})\text{TiCl}_2$	$\text{MgCl}_2 \cdot 0.22\text{AlEt}_{2,3}(\text{OEt})_{0.7}$	217	1579000	2.4
Cp_2ZrCl_2	$\text{MgCl}_2 \cdot 0.22\text{AlEt}_{2,3}(\text{OEt})_{0.7}$	114	897000	2.7

EXPERIMENTAL

Materials. All manipulations were performed under an argon atmosphere using glove box (Braun MB-150 GI or LM-130) and Schlenk techniques. Toluene and heptane were distilled from sodium and stored over 4 Å molecular sieves. Petroleum ether (b.p. 40–70°C) was passed over a column containing activated alumina. All solvents were freeze-thaw degassed twice before use. The various catalyst components used in this work were purchased or synthesized, as described previously [14–17].

Support preparation and catalyst immobilization. The $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ supports used in this work were prepared using methods similar to those described in [8]. Typically, 10–50 ml of *n*-heptane were added to 1–5 g of a spherical adduct of magnesium chloride and ethanol under argon and the mixture was cooled to 0°C. A 25–28 wt % solution of AlR_3 was then added gradually, over 5–10 min, to give a molar ratio $\text{AlR}_3/\text{EtOH} = 2$, the reaction being carried out in a standard Schlenk vessel equipped with a pressure release valve. The mixture was allowed to warm slowly to room temperature and the reaction was continued with occasional agitation for a further 2 days (AlEt_3) or 3 days ($\text{Al}(i\text{-Bu})_3$). The solid support was isolated by filtration, washed with heptane and petroleum ether, and then dried under a flow of argon and subsequently in vacuum.

Catalyst immobilization with these supports was carried out by heating a mixture of catalyst, support, and toluene (typically 10 ml/g support) to 50–60°C and reacting for 1–4 h, after which the liquid layer was

removed by decantation and the solid was dried under a flow of argon at 60°C.

Polymerization conditions. Ethylene polymerization was typically carried out in a 1-l autoclave by charging 100 mg of immobilized catalyst (containing 0.5–10 µmol Ti) to 450 ml petroleum ether or toluene, to which 1 mmol $\text{Al}(i\text{-Bu})_3$ had been added, at 50°C and an ethylene pressure of 5 bar. Polymerization was then carried out at either 5 or 10 bar for 1 h at 50°C.

Polymer characterization. Molecular weights and molecular weight distributions of the resulting polymers were determined by high temperature GPC (PL-GPC210) at 135°C using 1,2,4-trichlorobenzene as a

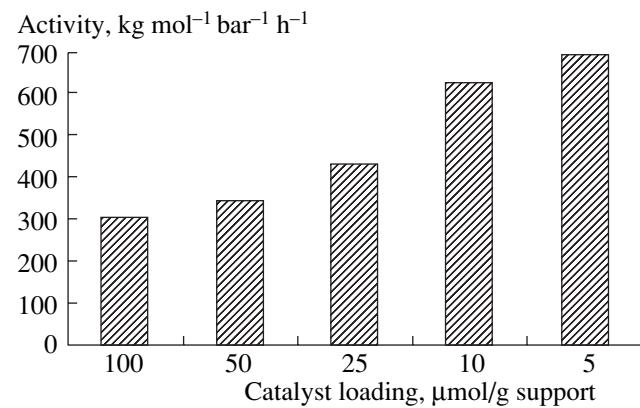


Fig. 1. Effect on polymerization activity of Cp_2TiCl_2 loading on support.

	1	2	3	4
Activity	1830	1230	2810	7940
\bar{M}_w	1601000	2494000	2004000	503000
\bar{M}_w/\bar{M}_n	3.1	2.0	3.3	2.5

Fig. 2. Ti-based single-site catalysts immobilized on $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ supports (polymerization activity in $\text{kg mol}^{-1} \text{bar}^{-1} \text{h}^{-1}$).

solvent and using narrow-molecular-weight-distribution polystyrene for calibration.

RESULTS AND DISCUSSION

The reaction between a MgCl_2 /ethanol adduct and excess aluminum alkyl generates alkylaluminum ethoxide species, most of which are washed out of the final solid product. However, on account of strong $\text{Mg}-\text{O}(\text{Et})-\text{Al}$ bridging, a significant quantity of the $\text{AlR}_n(\text{OEt})_{3-n}$ species formed is retained by the support. It can be seen from Table 1 that the content of alkylaluminum ethoxide species in the final support is higher with AlEt_3 than with $\text{Al}(i\text{-Bu})_3$ and increases with increasing ethanol content in the MgCl_2 /ethanol adducts used in support preparation. The particle sizes of the $\text{MgCl}_2/\text{EtOH}$ adducts used were in the range 10–100 μm and remained essentially unchanged throughout the support preparation.

Immobilization of Cp_2TiCl_2 and other metallocene and nonmetallocene catalyst components on

Table 3. Ethylene polymerization with immobilized catalysts $(\text{RCp})_n\text{TiCl}_{3-n}$

Catalyst	Activity, $\text{kg mol}^{-1} \text{bar}^{-1} \text{h}^{-1}$	\bar{M}_w	\bar{M}_w/\bar{M}_n
Cp_2TiCl_2	606	619000	2.3
CpTiCl_3	7510	1082000	2.2
$(i\text{-BuCp})\text{TiCl}_3$	7520	865000	2.4
$(\text{C}_5\text{Me}_5)\text{TiCl}_3$	5930	1767000	2.1
$(\text{Indenyl})\text{TiCl}_3$	9140	1624000	2.5
TiCl_4	25520	1600000	4.1

$\text{MgCl}_2/\text{alkylaluminum ethoxide}$ supports was carried out by treatment of the support with a toluene solution of the catalyst. An immediate green coloration of the support was observed on addition of the bright red solution of Cp_2TiCl_2 in toluene. Further reaction at 60°C resulted in complete discoloration of the liquid phase, indicating effective and quantitative immobilization of the metallocene on the support.

The results of ethylene polymerizations carried out using the quantitatively immobilized catalysts are given in Table 2. In these experiments, a small quantity of $\text{Al}(i\text{-Bu})_3$ was added to the polymerization medium in order to ensure effective scavenging of impurities. Comparison of the activities obtained using the various single-site catalyst components reveals that good activity was obtained both with Cp_2TiCl_2 and with the constrained geometry catalyst $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N}-i\text{-Bu})\text{TiCl}_2$, whereas Cp_2ZrCl_2 gave relatively low activity. The GPC data reveal narrow molecular weight distributions, with \bar{M}_w/\bar{M}_n in the range 2.0–2.8, indicative of retention of the single-site behavior of the catalyst despite the use of a magnesium chloride-based support. Previous studies have indicated that the polydispersity of polyethylene prepared using metallocenes on MgCl_2 supports can range from narrow to broad, depending on the catalyst immobilization approach used [3–5, 9, 18, 19].

Further experiments showed that catalyst activity increased as the loading of catalyst on the support was decreased. Figure 1 shows that a doubling in activity could be achieved in this way, and low catalyst loadings (typically 5 or 10 $\mu\text{mol/g}$ support) were subsequently used for the immobilization of a range of other catalysts on $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ supports.

Catalysts of type 1 and 2 in Fig. 2 have been shown to give activities of up to around 1600 $\text{kg mol}^{-1} \text{bar}^{-1} \text{h}^{-1}$

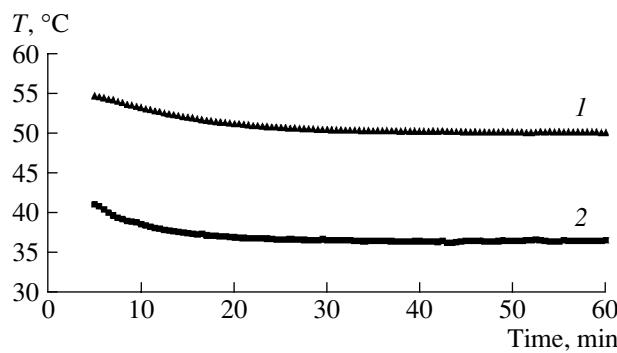


Fig. 3. Temperature profile of ethylene polymerization using $[(\text{Indenyl})\text{TiCl}_3]$ immobilized on a $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$ support: (1) internal temperature; (2) cooling mantle temperature.

under homogeneous polymerization conditions [20, 21]. The results in Fig. 2 show that similar activities can be obtained, without MAO or borate activator, after immobilization on magnesium chloride. Good activity is also apparent with the FI catalyst [22] 3, the effective activation of which with a MgCl_2 -based support has previously been demonstrated by Fujita and coworkers [12, 13]. Catalyst 4 has been shown by Deckers et al. [23] to be effective for the trimerization of ethylene to 1-hexene under homogeneous conditions with MAO and also when immobilized and activated using a SiO_2/MAO support. However, the data in Fig. 2 show that immobilization on a $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ support leads to a highly active polymerization system. No evidence for 1-hexene formation was found, and the transformation from a trimerization to a polymerization system indicates that coordination of the pendant aryl ring to the metal center, an essential feature of the trimerization mechanism [23, 24], is no longer operative.

The results of immobilization and activation of CpTiCl_3 and related precatalysts on a support of composition $\text{MgCl}_2 \cdot 0.14\text{AlEt}_{2.2}(\text{OEt})_{0.8}$ are given in Table 3, from which it is apparent that high activities of around $6000\text{--}9000 \text{ kg mol}^{-1} \text{ bar}^{-1} \text{ h}^{-1}$ were obtained. Excep-

tionally high activity was obtained using TiCl_4 , but in this case a broader molecular weight distribution was obtained, signifying that this is no longer a single-site system and that in this series we are at the border of single-site and Ziegler–Natta catalysis. There was no evidence for catalyst deactivation during the course of any of these polymerizations. A typical plot illustrating this is given in Fig. 3, from which an essentially constant rate of polymerization is evident from the constant temperature difference between the reactor contents and the cooling mantle. Furthermore, spherical polymer particle morphology was obtained without reactor fouling, as illustrated by the scanning electron micrographs in Fig. 4, which reveal that the spherical morphology of the original support has been retained and replicated throughout catalyst immobilization and polymerization.

Following the above studies, we decided to investigate the effectiveness of these spherical supports for the immobilization and activation of other early- and late-transition-metal catalysts, such as the chromium and nickel complexes shown in the scheme. The MAO-activated polymerization of ethylene with the chromium(III) complex 5 has been described by Jolly and coworkers [25, 26]. In the present work, immobilization of this complex on a support of composition $\text{MgCl}_2 \cdot 0.14\text{AlEt}_{2.2}(\text{OEt})_{0.8}$ resulted in an ethylene polymerization activity of $2690 \text{ kg mol}^{-1} \text{ bar}^{-1} \text{ h}^{-1}$, comparable to the activities obtained under homogeneous conditions using MAO. The single-site characteristics of the immobilized system were apparent from both GPC data ($\bar{M}_w/\bar{M}_n = 1.8$) and rheological properties of the polyethylene obtained [17]. It is believed that this is the first example of a high-activity, heterogeneous chromium-based system exhibiting genuinely single-site behavior in ethylene polymerization.

Recently, there has been increasing interest in late-transition-metal catalysts for the polymerization of olefins, following the discovery by Brookhart and coworkers of aryl-substituted α -diimine nickel(II) and palladium(II) complexes able to polymerize ethylene to give

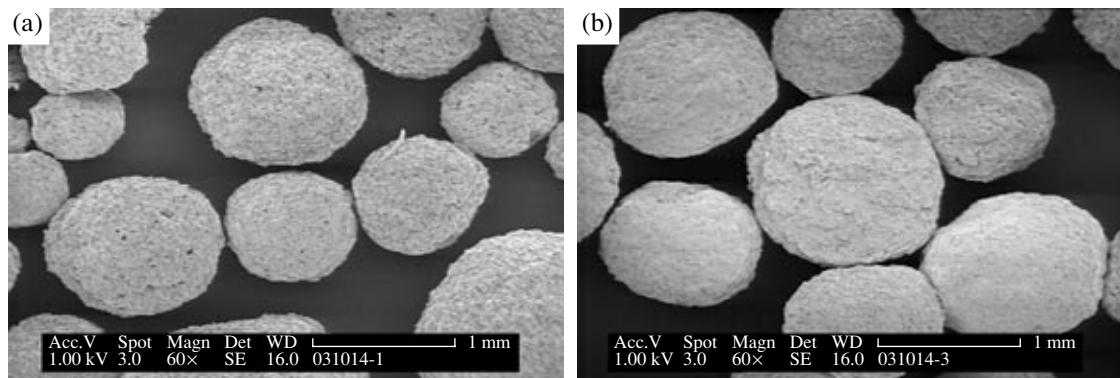
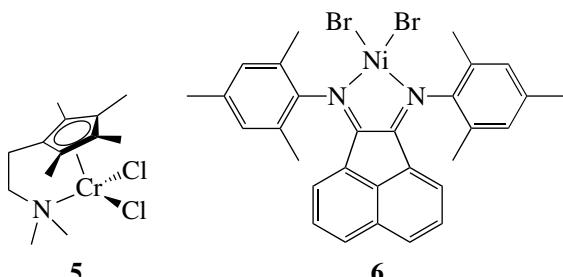


Fig. 4. Scanning electron micrographs of polyethylene prepared using catalysts immobilized on a $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ support: (a) $(t\text{-BuCp})\text{TiCl}_3$; (b) TiCl_4 .



Scheme. Chromium and nickel complexes used in catalyst immobilization.

new types of polyethylene with substantial chain branching [27–29]. The polymer chain microstructure is dependent on the steric bulk of the ortho substituents on the aryl rings and on the polymerization conditions, chain branching increasing with increasing temperature and decreasing ethylene pressure. In the present work, a support of composition $MgCl_2 \cdot 0.24AlEt_{2,3}(OEt)_{0.7}$ was used to support various Ni diimine complexes. Very high ethylene polymerization activity was obtained with complex **6**. The productivity in a 1-h polymerization at 50°C was 7160 kg mol⁻¹ bar⁻¹ h⁻¹, significantly higher than the productivities previously reported [30, 31] for this and analogous complexes under homogeneous polymerization conditions or immobilized on silica. As is the case in homogeneous polymerization with Ni diimine complexes, the degree of chain branching is strongly influenced by the nature of the substituents in the ortho positions of the aryl rings. The polyethylene prepared with the $MgCl_2$ -immobilized complex **6** contained 7 branches per 1000 carbon atoms, whereas a complex with the same α -diimine backbone but with 2,6-diisopropyl substituents in the aryl rings gave 24 branches per 1000 carbon atoms [16]. Again, narrow polydispersities ($\bar{M}_w/\bar{M}_n = 2.1$ –2.9) were obtained, indicating that the single-site characteristics of these catalysts are unaffected by immobilization on the support. Magnesium chloride-based supports have now also been used for the immobilization of iron-based catalysts for polyethylene [32, 33], providing a further demonstration of the usefulness and versatility of such supports for the immobilization of homogeneous catalysts.

CONCLUSIONS

The use of spherical supports of type $MgCl_2/AlR_n(OEt)_{3-n}$, obtained by reaction of AlR_3 with adducts of magnesium chloride and ethanol, offers a simple and effective approach for the immobilization of a broad range of single-site catalysts for olefin polymerization, without the use of methylaluminoxane or borate activators. The method is effective for both early- and late-transition-metal catalysts and in many cases leads to significantly higher activities than have been reported for homogeneous polymerization. This is

to a large extent due to the stabilizing effect of the $MgCl_2$ -based support, leading to negligible catalyst decay during polymerization. The particle morphology of the starting support is retained and replicated throughout the catalyst immobilization and polymerization, giving spherical polymer particle morphology with no reactor fouling.

REFERENCES

1. Hlatky, G.G., *Chem. Rev.*, 2000, vol. 100, no. 4, p. 1347.
2. Marks, T.J., *Acc. Chem. Res.*, 1992, vol. 25, no. 2, p. 57.
3. Kaminaka, M. and Soga, K., *Makromol. Chem., Rapid Commun.*, 1991, vol. 12, p. 367.
4. Soga, K. and Kaminaka, M., *Macromol. Chem. Phys.*, 1994, vol. 195, p. 1369.
5. Kissin, Y.V., Nowlin, T.E., Mink, R.I., and Brandolini, A.J., *Macromolecules*, 2000, vol. 33, no. 12, p. 4599.
6. Satyanarayana, G. and Sivaram, S., *Macromolecules*, 1993, vol. 26, no. 17, p. 4712.
7. Moore, E.P., *Polypropylene Handbook*, Munich: Hanser, 1996.
8. US Patent 5698487, 1995.
9. Silveira, F.D., Forte, M.C., Santos, J.H.Z., Stedile, F.C., and Zacca, J.J., *Polim.: Cienc. Tecnol.*, 2000, vol. 10, no. 1, p. 42.
10. Guan, Z., Zheng, Y., and Jiao, S., *J. Mol. Catal. A: Chem.*, 2002, vol. 188, nos. 1–2, p. 123.
11. Cho, H.S. and Lee, W.Y., *J. Mol. Catal. A: Chem.*, 2003, vol. 191, no. 2, p. 155.
12. Nakayama, Y., Bando, H., Sonobe, Y., Kaneko, H., Kashiiwa, N., and Fujita, T., *J. Catal.*, 2003, vol. 215, no. 1, p. 171.
13. Nakayama, Y., Bando, H., Sonobe, Y., and Fujita, T., *Bull. Chem. Soc. Jpn.*, 2004, vol. 77, p. 617.
14. Severn, J.R. and Chadwick, J.C., *Macromol. Rapid Commun.*, 2004, vol. 25, no. 10, p. 1024.
15. Severn, J.R. and Chadwick, J.C., *Macromol. Chem. Phys.*, 2004, vol. 205, no. 15, p. 1987.
16. Severn, J.R., Chadwick, J.C., and van Axel Castelli, V., *Macromolecules*, 2004, vol. 37, no. 17, p. 6258.
17. Severn, J.R., Kukalyekar, N., Rastogi, S., and Chadwick, J.C., *Macromol. Rapid Commun.*, 2005, vol. 26, no. 3, p. 150.
18. Sensarma, S. and Sivaram, S., *Polymer Int.*, 2002, vol. 51, no. 5, p. 417.
19. Int. Patent WO 01/46271, 2000.
20. Kretschmer, W.P., Dijkhuis, C., Meetsma, A., Hessen, B., and Teuben, J.H., *Chem. Commun.*, 2002, no. 6, p. 608.
21. Stephan, D.W., Stewart, J.C., Guerin, F., Courtenay, S., Kickham, J., Hollink, E., Beddle, C., Hoskin, A., Graham, T., Wei, P., Spence, R.E.V.H., Xu, W., Koch, L., Gao, X., and Harrison, D.G., *Organometallics*, 2003, vol. 22, no. 9, p. 1937.
22. Saito, J., Mitani, M., Matsui, S., Tohi, Y., Makio, H., Nakano, T., Tanaka, H., Kashiiwa, N., and Fujita, T., *Macromol. Chem. Phys.*, 2002, vol. 203, no. 1, p. 59.
23. Deckers, P.J.W., Hessen, B., and Teuben, J.H., *Organometallics*, 2002, vol. 21, no. 23, p. 5122.

24. Blok, A.N.J., Budzelaar, P.H.M., and Gal, A.W., *Organometallics*, 2003, vol. 22, no. 13, p. 2564.
25. Emrich, R., Heinemann, O., Jolly, P.W., Krüger, C., and Verhovnik, G.P.J., *Organometallics*, 1997, vol. 16, no. 8, p. 1511.
26. Döring, A., Göhre, J., Jolly, P.W., Kryger, B., Rust, J., and Verhovnik, G.P.J., *Organometallics*, 2000, vol. 19, no. 4, p. 388.
27. Johnson, L.K., Killian, C.M., and Brookhart, M., *J. Am. Chem. Soc.*, 1995, vol. 117, no. 23, p. 6414.
28. Ittel, S.D., Johnson, L.K., and Brookhart, M., *Chem. Rev.*, 2000, vol. 100, no. 4, p. 1169.
29. Gibson, V.C. and Spitzmesser, S.K., *Chem. Rev.*, 2003, vol. 103, no. 1, p. 283.
30. Maldanis, R.J., Wood, J.S., Chandrasekaran, A., Rausch, M.D., and Chien, J.C.W., *J. Organomet. Chem.*, 2002, vol. 645, nos. 1–2, p. 158.
31. Preishuber-Pfugl, P. and Brookhart, M., *Macromolecules*, 2002, vol. 35, no. 16, p. 6074.
32. Huang, R., Liu, D., Wang, S., and Mao, B., *Macromol. Chem. Phys.*, 2004, vol. 205, no. 7, p. 966.
33. Mikenas, T.B., Zakharov, V.A., Echevskaya, L.G., and Maksko, M.A., *J. Polym. Sci., Part A: Polym. Chem.*, 2005, vol. 43, no. 10, p. 2128.