1,4-*Cis* Selectivity and Molecular Weight Control of Polymer in the Polymerization of 1,3-Butadiene with Metallosalen Complexes/Methylaluminoxane Catalysts

Kiyoshi ENDO* and Takahiro KITAGAWA

Department of Bio-Applied and Applied Chemistry, Graduate School of Engineering, Osaka City University,
Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

* Corresponding author: endo@a-chem.eng.osaka-cu.ac.jp

Received January 15, 2005; Accepted April 17, 2005
© 2005 The Society of Rubber Industry, Japan

Abstract 1,4-*Cis*-selective and molecular weight control of the polymer in the polymerization of butadiene (Bd) with various metallosalen [metal=Co, Ni, Fe, V, Ti; salen=*N,N'*-bis(salicylidene)ethylenediamine] in combination with methylaluminoxane (MAO) was investigated. The activity for the polymerization of Bd was influenced by both substituents of the salen ligands and mixing order of reagents. The activity for the polymerization of Bd with metallosalen complexes activated by MAO in the presence of Bd was higher than that in the absence of Bd. By introducing the *tert*-butyl group in the aromatic ring of salen, the activity for the polymerization of Bd increased, but the microstructure of the poly(Bd) did not change significantly. Among the metallosalen complexes examined, *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)ethylenediaminato Co(II) (**1-Co**) complex in combination with MAO gave the high molecular weight polymer with highest 1,4-*cis* content. Molecular weight control of the polymer was achieved by the polymerization of Bd with **1-Co**/MAO catalyst.

Keywords Butadiene, Polymerization, High 1,4-*cis*, Metallosalen complexes, *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-ethylenediaminato cobalt(II), Molecular weight control.

Introduction

Butadiene (Bd) is an important monomer used as a basic chemical of synthetic rubbers such as butadiene rubber (BR) and styrene-butadiene rubber (SBR) which are important polymers for rubber industry. Poly(Bd) has four kinds of microstructures; 1,4-*cis*, 1,4-*trans*, 1,2-syndiotactic, 1,2-isotactic, and physical and mechanical properties of the polymer depend strongly on the microstructures¹. Namely, 1,2-syndiotactic poly(Bd) is crystalline resin, and the melting point of the polymer changes from 70 to 216°C according to a difference in crystallinity. 1,4-*Trans* polymer is also resin which melts at 100–141°C. 1,4-*Cis* poly(Bd) has rubber elasticity, and high 1,4-*cis* poly(Bd) is used for tire material, and low 1,4-*cis* poly(Bd) is utilized as a modifier for impact absorber of polyethylene. The materials having good physical and mechanical properties can be obtained by choosing adequate catalysts through precisely controlled polymerization of Bd.

Metallocene catalysts make it possible to control of

stereoregularity of polymer by designing ligands of catalysts². Moreover, homogeneous post-metallocene catalysts such as Ni(II) di-imine complexes^{3,4}, Ti(IV) di-amide complexes⁵, and Ni(II) imin-pyridine complexes^{6,7} have been discovered, in which they show a high activity for polymerization of olefin and other monomers.

On the other hand, high 1,4-*cis* polymerization of butadiene (Bd) with Ziegler–Natta catalysts such as $\text{TiI}_4/\text{AlR}_3$ ⁸, $\text{CoCl}_2 \cdot (\text{pyridine})_2/\text{AlEt}_2\text{Cl}$ ⁹, $(\eta^3\text{-C}_3\text{H}_5)\text{Ni}(\text{OCOCF}_3)$ ¹⁰, and $\text{Nd}(\text{carboxylate})_3/\text{AlEt}_2\text{Cl}/\text{Al}(i\text{-Bu})_3$ ¹¹ have been reported. Metallocene complexes in combination with methylaluminoxane (MAO) are also effective catalysts for producing a high 1,4-*cis* polymer in the polymerization of 1,3-dienes. Such examples were found in the polymerization with CpTiCl_3 ¹², $\text{CpVCl}_2(\text{PEt}_3)_2$ and Cp_2VCl ¹³ to give the polymers consisting of mainly 1,4-*cis* units.

Among many transition metal complexes, metallosalen complexes are known to be useful as catalysts for an asymmetric epoxidation¹⁴. However, some of them have been utilized as polymerization catalysts in an

oligomerization of ethylene with zirconium-salen complex¹⁵, a polymerization of norbornene with nickel-salen complex/MAO¹⁶, and a polymerization of propylene with MgCl₂-supported 1,2-cyclohexanediamino-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)manganese chloride activated by AlEt₃Cl to give an atactic polymer with a high molecular weight¹⁷. However, there are few reports on polymerizations of 1,3-dienes with metallocene complexes. An example is found in the literature for the polymerization of Bd with 1,2-cyclohexanediamino-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)Ni/BF₃OBu₂/MAO catalyst to give 1,4-*cis* poly(Bd)¹⁸. These results suggest that various metallocene complexes are capable of effective catalysts for the polymerization of Bd to produce high 1,4-*cis* polymer by designing the ligand of salen, although detailed study for the polymerization of Bd with metallocene complexes in combination with MAO has not been investigated.

In this article, we report on the polymerization of Bd with metallocene complexes. Moreover, the molecular weight control of the polymer will be described in the polymerization of Bd with *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)ethylenediaminato Co(II) (**1-Co**)/MAO catalysts.

Experimental

Materials

Bd was purified by distillation over calcium hydride before use. Commercially available Ni(II)(salen) and Co(II)(salen) were used as received. MAO diluted with toluene kindly supplied from Tosoh Co. was used as received. Solvents were used after purification by conventional methods. Other chemicals were obtained commercially and used as received.

N,N'-Bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine (**1**)

To a solution of 3,5-di-*tert*-butylsalicylaldehyde (1.5 g, 6.4 mmol) in methanol (50 ml) was added ethylenediamine (0.192 g, 3.2 mmol). The mixture was stirred at room temperature for 2 h and then filtered off. After filtration the light-yellow powder was washed with a small amount of cold hexane and dried under vacuum to give 1.33 g (78.5%) of *N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine (**1**). mp 188–189°C. ¹H NMR (CDCl₃): δ 13.64 (1H, OH), 8.38 (1H, ArCH=N), 7.35 (1H, ArH), 7.25 (1H, ArH), 3.91 (2H, CH₂N), 1.42 (9H, *t*-Bu-*Me*), 1.27 (9H, *t*-Bu-*Me*). IR (KBr) 3422 (ν_{O-H}), 1628 (ν_{C=N}) cm⁻¹.

N,N'-Bis(3,5-di-*tert*-butylsalicylidene)ethylenediaminato nickel(II) (**1-Ni**)

To a solution of **1** (1.2 g, 2.4 mmol) was added Ni(OAc)₂·4H₂O (0.607 g, 2.4 mmol). The mixture was refluxed for 2 h and then filtered off. After filtration the dark yellow needles were washed with a small amount of cold methanol and dried under vacuum to give 1.31 g (72.7%) of **1-Ni**. ¹H NMR (CDCl₃): δ 7.49 (1H, ArCH=N), 7.30 (1H, ArH), 6.87 (1H, ArH), 3.30 (2H, CH₂N), 1.16 (9H, *t*-Bu-*Me*). IR (KBr) 1621 (ν_{C=N}) cm⁻¹.

N,N'-Bis(3,5-di-*tert*-butylsalicylidene)ethylenediaminato cobalt(II) (**1-Co**)

N,N'-Bis(3,5-di-*tert*-butylsalicylidene)ethylenediaminato cobalt(II) (**1-Co**) was prepared from an equimolar amount of **1** and Co(OAc)₂·4H₂O in a similar manner to that for **1-Ni** (orange powder, 71.1%). ¹H NMR (CDCl₃): δ 7.51 (1H, ArCH=N), 7.06 (1H, ArH), 6.99 (1H, ArH), 3.92 (2H, CH₂N), 1.43 (9H, *t*-Bu-*Me*), 1.28 (9H, *t*-Bu-*Me*). IR (KBr) 1596 (ν_{C=N}) cm⁻¹.

N,N'-Bis(3,5-di-*tert*-butylsalicylidene)ethylenediaminato iron(III) (**1-Fe**)

N,N'-Bis(3,5-di-*tert*-butylsalicylidene)ethylenediaminato iron(III) (**1-Fe**) was prepared from an equimolar amount of **1** and FeSO₄·7H₂O in a similar manner to that for **1-Ni** (dark-purple powder, 67.5%). ¹H NMR (CDCl₃): δ 8.33 (1H, ArCH=N), 7.60 (1H, ArH), 7.31 (1H, ArH), 4.20 (2H, CH₂N), 1.51 (9H, *t*-Bu-*Me*), 1.32 (9H, *t*-Bu-*Me*). IR (KBr) 1621 (ν_{C=N}) cm⁻¹.

N,N'-Bis(3,5-di-*tert*-butylsalicylidene)ethylenediaminato titanium(IV) dichloride (**1-Ti**)

N,N'-Bis(3,5-di-*tert*-butylsalicylidene)ethylenediaminato titanium dichloride (**1-Ti**) was prepared from an equimolar amount of **1** and TiCl₄ in a similar manner to that for **1-Ni** under nitrogen atmosphere (red powder, 49.3%). ¹H NMR (CDCl₃): δ 7.74 (1H, ArCH=N), 7.52 (1H, ArH), 7.00 (1H, ArH), 3.92 (2H, CH₂N), 1.53 (9H, *t*-Bu-*Me*), 1.36 (9H, *t*-Bu-*Me*). IR (KBr) 1617 (ν_{C=N}) cm⁻¹.

N,N'-Bis(3,5-di-*tert*-butylsalicylidene)ethylenediaminato vanadium(III) chloride (**1-V**)

N,N'-Bis(3,5-di-*tert*-butylsalicylidene)ethylenediaminato vanadium chloride (**1-V**) was prepared by the reaction of **1** and VCl₃ in a similar manner to that for **1-Ni** (red powder, 49.3%). ¹H NMR (CDCl₃): δ 7.49 (1H, ArCH=N), 7.30 (1H, ArH), 6.87 (1H, ArH), 3.30 (2H, CH₂N), 1.40 (9H, *t*-Bu-*Me*), 1.25 (9H, *t*-Bu-*Me*). IR (KBr) 1617 (ν_{C=N}) cm⁻¹.

Polymerization procedure

Polymerization was carried out in a sealed glass tube with a rubber septum with a connection to a vacuum system. After purging the tube with nitrogen, 8 ml of CH_2Cl_2 solution of complex, 1 ml of Bd and 1 ml of MAO solution was charged into the tube in this order. Bd monomer was charged at -78°C by a vacuum distillation over calcium hydride. Then the tube was sealed under high vacuum. The polymerization was carried out in a thermostat at a constant temperature for a given time. After polymerization, the tube was opened, and the contents of the tube were poured into a 200 ml of methanol containing a small amount of hydrochloric acid and *p*-*tert*-butylphenol to precipitate the polymer formed. The polymers was washed with methanol and dried in vacuo. Polymer yield was calculated by gravimetry.

Characterization of polymers

Number average molecular weight (M_n) and weight average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the polymer were estimated by gel permeation chromatography (GPC) using a Tosoh 8000 series system in tetrahydrofuran as calibrated with polystyrene standards. The microstructure of poly(Bd) was determined from ^1H and ^{13}C NMR spectra taken in *d*-chloroform solvent at 20°C on a JEOL α -400NMR spectrometer.

Results and Discussion

Polymerization of Bd with metallasalen/MAO catalyst

In the polymerization of Bd with transition metal complexes, ligands of the metal complexes play a role to determine both activities for polymerization and 1,4-*cis* content.¹⁾ For this purpose, late transition metal complexes bearing the salen ligand introduced *tert*-butyl group in the aromatic ring of salen were synthesized, i.e., *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)ethylenediaminato nickel(II) (**1-Ni**) and *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-ethylenediaminato cobalt(II) (**1-Co**) as shown in Figure 1

was synthesized and compared with (salen)Ni(II) and (salen)Co(II), in which the metallasalen complexes were activated with MAO in the absence of Bd. The polymerization of Bd with these complexes in combination with MAO was conducted. The results are listed in Table 1. In a preliminary experiment, polymerization of Bd was tested. The polymerization proceeded smoothly in CH_2Cl_2 , but the polymerization did not gave almost no polymer in toluene. This may be explained by that (salen)Ni(II) is soluble in CH_2Cl_2 , but insoluble in toluene. Thus, CH_2Cl_2 was used as the polymerization solvent in this study. The activity for polymerization of Bd with (salen)Ni(II) and (salen)Co(II) complexes bearing ligand **1** introduced *tert*-butyl group was higher than that with (salen)Ni(II)/MAO and (salen)Co(II)/MAO catalysts.

Effect of mixing order of the reagents

A mixing order of the reagents was reported to play an important role to determine the activity for polymerization of Bd with binary catalysts¹⁾. In the polymerization of Bd with $\text{V}(\text{acac})_3/\text{MAO}$ catalyst, the microstructure of polymer and the activity for the polymerization was reported to depend strongly on a mixing order of reagents including Bd monomer^{13,19)}. Moreover, in the polymerization of Bd with $\text{Co}(\text{acac})_3/\text{MAO}$ catalyst, the rate of polymerization increased with an addition of MAO to Co complex in the presence of Bd^{20–22)}. To check this point in the polymerization of Bd with **1-Co**/MAO or **1-Ni**/MAO catalyst, the various mixing order of metallasalen

Figure 1. Synthesis of the metallasalen complexes.

Table 1. Polymerization of Bd with metallasalen/MAO catalyst in CH_2Cl_2 at 20°C

Metallasalen	Time (h)	Polymer yield (%)	$M_n \times 10^{-4}$	M_w/M_n	Microstructure (%)		
					1,4- <i>cis</i>	1,4- <i>trans</i>	1,2-vinyl
Ni(salen)	16	43.8	2.3	2	85	9.7	5.3
1-Ni	1	79.5	2.2	3	92.3	4.1	3.6
Co(salen)	3	8.9	2.9	2	92.5	4.3	3.2
Co(salen)	24	34.9	2.7	3.6	91.8	4.8	3.4
1-Co	12	31.2	4.7	3.3	96.6	~0	3.4

[Bd] = 1.2 mol/L, [Metal] = 6.7×10^{-4} mol/L, MAO/Metal = 500 mole ratio.

Table 2. Effect of mixing order of the reagents on polymerization of Bd with metallocalen/MAO catalyst in CH₂Cl₂ at 20°C

Mixing order	Time (h)	Polymer yield (%)	$M_n \times 10^{-4}$	M_w/M_n	Microstructure (%)		
					1,4- <i>cis</i>	1,4- <i>trans</i>	1,2-vinyl
Ni→MAO→Bd	1	79.5	2.2	3	92.3	4.1	3.6
Ni→Bd→MAO	1	81.5	1.7	2.6	93.1	4.8	2.1
Co→MAO→Bd	6	trace	—	—	—	—	—
Co→Bd→MAO	0.5	81.2	8.9	3.3	96.7	~0	3.3

[Bd] = 1.2 mol/L, [Metal] = 6.7×10^{-4} mol/L, MAO/Metal = 500 mole ratio.

Table 3. Polymerization of Bd with metallocalen/MAO catalyst in CH₂Cl₂ at 20°C

1-M	Time (h)	Polymer yield (%)	$M_n \times 10^{-4}$	M_w/M_n	Microstructure (%)		
					1,4- <i>cis</i>	1,4- <i>trans</i>	1,2-
1-Ni	1	79.5	2.2	3	92.3	4.1	3.6
1-Co	0.5	81.2	8.9	3.3	96.7	~0	3.3
1-Fe	1	17.3	7	2.7	82.2	7.3	10.5
1-V	6	9.9	1.5	1.3	~0	90.5	9.5
1-Ti	3	trace	—	—	—	—	—

[Bd] = 1.2 mol/L, [M] = 6.7×10^{-4} mol/L, MAO/Metal = 500 mole ratio.

The reagents were charged in order of metal complex, Bd and MAO.

complex, Bd, and MAO was changed. Namely, the metallocalen complex was activated by MAO in the presence or absence of Bd monomer. The results for **1-Ni**/MAO and **1-Co**/MAO catalyst systems are shown in Tables 2. Effect of a mixing order of reagents on the activity for polymerization of Bd with **1-Co**/MAO was observed. The activity for the polymerization of Bd with **1-Co**/MAO activated by MAO in the presence of Bd monomer was found to be higher than that activated in the absence of Bd. The effect of mixing order of the reagents on the polymerization may be explained by a difference in the stability of the Co complex in the presence and absence of Bd as illustrated in Figure 2. In the polymerization of Bd with the catalyst prepared in the presence of Bd, π -electrons from the alkenyl group can be donated into the vacant d orbital of the Co atom to stabilize the Co–C bond. Alternatively, when the ligand is the alkenyl group, π -allyl bond can form easily to stabilize the active site for polymerization¹⁾. In the absence of Bd such stabilization may be operated to lead the reduction of zerovalent Co or decomposition of the Co complex¹⁾.

On the other hand, the activity for the polymerization of Bd with **1-Ni**/MAO catalyst was not affected by the mixing order of the reagents as shown in Table 2. Although the reason for a difference in the activity for the polymerization of Bd between **1-Ni** and **1-Co** is not clear, the stability of Ni–C bond may be different from that of Co–C bond.

In the presence of Bd

Figure 2. Active site formation of Co complex activated by MAO in the presence of butadiene.

Polymerization of Bd with 1-Metal/MAO catalysts

In the polymerization of Bd with transition metal catalysts, it is known that a microstructure of polymer and an activity for the polymerization are strongly dependent on the central metal^{19–22)}. To check this point in the polymerization of Bd with metallocalen/MAO catalysts, some transition metallocalen complexes in addition to **1-Ni** and **1-Co** complexes were synthesized as shown in Figure 1, and the polymerization of Bd with these metallocalen complexes was examined. The results for the polymerization of Bd with transition metallocalen complexes bearing the same ligand **1** in combination with MAO are listed in Table 3. The activity for the polymerization of Bd was found to depend strongly on the center metal examined. On concerning the central metal, the activity for the polymerization of Bd decreased with the following order: **1-Co** > **1-Ni** > **1-Fe** > **1-V** > **1-Ti**. Namely, late transition metallocalen complexes showed a high activity for the polymerization of Bd. The GPC elution curves of polymers obtained with these catalysts

Figure 3. ^1H and ^{13}C NMR spectra of poly(butadiene) obtained with **1-Co**/MAO catalyst.

were unimodal, suggesting that the polymerization of Bd proceeds with a single active site.

The microstructure of the polymers obtained from the polymerization of Bd with metallocalen/MAO catalyst was determined using ^1H and ^{13}C NMR spectra of the polymers. The typical ^1H and ^{13}C NMR spectra of the polymers are shown in Figure 3. In accordance with the activity for the polymerization, the 1,4-*cis* content of the polymer obtained with late transition metals was higher than these obtained with early transition metal complexes such as **1-Ti**/MAO catalyst and **1-V**/MAO catalyst, which is in a good agreement with the results reported previously for the polymerization of Bd with metal(acac)_x/MAO catalysts¹⁹.

Since **1-Co**/MAO and **1-Ni**/MAO gave a polymer with high 1,4-*cis* content in a good yield, the polymerization of Bd with these catalysts was investigated in detail. The polymerization of Bd with **1-Metal**/MAO (Metal: Ni, Co) catalysts activated by MAO in the presence of Bd monomer was conducted. The results using (salen)Ni(II)/MAO catalyst and (salen)Co(II) catalyst are shown in Figures 4 and 5, respectively. The results for the polymerization of (salen)Ni(II)/MAO catalyst and (salen)Co(II) catalyst are also indicated for comparison. When **1-Ni**/MAO and **1-Co**/MAO were used as catalysts,

Figure 4. Polymerization of butadiene (Bd) with Ni complex/MAO catalyst in CH_2Cl_2 at 20°C ; $[\text{Bd}] = 1.2 \text{ mol/L}$, $[\text{Ni}] = 6.7 \times 10^{-4} \text{ mol/L}$, $\text{MAO}/\text{Ni} = 500$ mole ratio, (●) **1-Ni**, (○) (salen)Ni(II). The reagents were charged in the order of Ni complex, Bd, and MAO.

Figure 5. Polymerization of butadiene (Bd) with Co complex/MAO catalyst in CH_2Cl_2 at 20°C ; $[\text{Bd}] = 1.2 \text{ mol/L}$, $[\text{Co}] = 6.7 \times 10^{-4} \text{ mol/L}$, $\text{MAO}/\text{Co} = 500$ mole ratio, (●) **1-Co**, (○) (salen)Co(II). The reagents were charged in the order of Co complex, Bd, and MAO.

the polymerization rates of Bd with these catalysts were accelerated remarkably as compared with those by the (salen)Ni(II)/MAO catalyst and the (salen)Co(II)/MAO catalyst. This may be explained by the distortion of the coplanarity between the central metal and the ligands of the salen from the analysis of X-ray powder diffraction pattern of the complexes, which has relation with the formation of an active site by reaction of the ligand and MAO to give a metal-methyl bond.

Molecular weight control with 1-Co/MAO catalyst

A simultaneous control of molecular weight of polymer and microstructure of polymer in the polymerization of Bd with $\text{Co}(\text{acac})_3/\text{MAO}$ catalyst was reported²². Since high 1,4-*cis* poly(Bd) was obtained in the polymerization of Bd with a 1-M/MAO ($\text{M}=\text{Ni}, \text{Co}$) catalysts as mentioned above, the control of the molecular weight of poly(Bd) obtained with these catalysts was examined. The relationship between M_n of the polymers and polymer yields are depicted in Figure 6. In the polymerization of Bd with 1-Ni/MAO catalyst, the molecular weights of the polymers did not change by reaction time, which is in a good agreement with that the polymerization of Bd with $\text{Ni}(\text{acac})_2/\text{MAO}$ catalyst as reported in a previous paper²³.

On the other hand, in the polymerization with 1-Co/MAO, the molecular weights of the polymers increased with an increase of polymer yields, and the line passed through the origin. Moreover, the molecular weights of the polymers were in a good agreement with the values obtained assuming the catalyst efficiency is unity. These results indicate that the polymerization of Bd with 1-Co/MAO has a living nature. Although, the molecular weight distribution (M_w/M_n) is not narrow, but the values of M_w/M_n kept almost constant at around 3 throughout reactions. This may be due to the slow initiation of the polymerization. In contrast to the polymerization of Bd with 1-Ni/MAO catalyst, the polymerization of Bd with 1-Co complexes was found to be possible to control both the molecular weight of the poly(Bd) and 1,4-*cis* selectivity.

Conclusion

In the polymerization of Bd with metallocene complexes in combination with MAO, 1-Co/MAO catalyst and 1-Ni/MAO catalysts showed high activities for the polymerization. High 1,4-*cis* polymer was obtained with the use of the catalysts, especially, 1-Co/MAO catalyst. The activity for the polymerization was influenced by substitution of the ligand of salen and mixing order of the reagents. The polymerization rate of Bd with 1-Co activated by MAO in the presence of Bd monomer was higher than that with simple metallocene complexes, because of distortion of coplanarity between the central Co and the ligand of salen. The molecular weight control of the polymer is possible in the polymerization of Bd with 1-Co/MAO catalyst.

References

- 1) Boor J. Jr.: "Ziegler-Natta Catalysts and Polymerizations" Academic Press, New York, (1979), Chap. 5.

Figure 6. Relationship between polymer yield and M_n for the polymerization of butadiene (Bd) with metallocene/MAO catalyst in CH_2Cl_2 at 20°C ; $[\text{Bd}]=1.2\text{ mol/L}$, $[\text{Metal}]=6.7\times 10^{-4}\text{ mol/L}$, $\text{MAO/Metal}=500$ mole ratio, (●) 1-Co, (○) 1-Ni. The reagents were charged in the order of metal complex, Bd, and MAO.

- 2) Kaminsky W., Arndt M.: *Adv. Polym. Sci.*, **127**, 143 (1996).
- 3) Johnson L. K., Killian C. M., Brookhart M.: *J. Am. Chem. Soc.*, **117**, 6414 (1995).
- 4) Johnson L. K., Mecking S., Brookhart M.: *J. Am. Chem. Soc.*, **118**, 267 (1996).
- 5) Scollard J. D., McConville D. H.: *J. Am. Chem. Soc.*, **118**, 10008 (1996).
- 6) Small B. L., Brookhart M., Bennet M. A.: *J. Am. Chem. Soc.*, **120**, 4049 (1998).
- 7) Britvsek G. J. P., Gibson V. C., Kimberley B. S., Maddox J., McTavish S. J., Solan G. A., White A. P., Williams D. J.: *Chem. Commun.*, 849 (1998).
- 8) Saltman W. M.: *Ind. Eng. Chem. Prod. Res. Dev.*, **3**, 199 (1964).
- 9) Gippin M.: *Ind. Eng. Chem. Prod. Res. Dev.*, **1**, 32 (1962).
- 10) Dawans F., Teyssie Ph.: *J. Polym. Sci. Polym. Lett.*, **7**, 111 (1969).
- 11) Oehme A., Gebauer U., Gehrke K., Lechner M. D.: *Angew. Makromol. Chem.*, **235**, 121 (1996).
- 12) Oliva L., Longo P., Grassi A., Ammendola P., Pellicchia C.: *Makromol. Chem. Rapid Commun.*, **11**, 519 (1990).
- 13) Ricci G., Panagia A., Porri L.: *Polymer*, **37**, 363 (1996).
- 14) Katsuki T.: *Curr. Org. Chem.*, **5**, 663 (2001).
- 15) Wang M., Zhu H. J., Jin K.: *J. Catal.*, **220**, 392 (2003).
- 16) Borker S., Saxena P.K.: *Polym. Bull.*, **44**, 167 (2000).
- 17) Ban H., Kase T., Murata M.: *J. Polym. Sci. A*, **39**, 3733 (2001).
- 18) Kwag G., Jang Y., Lee H.: *Polym. J.*, **31**, 1274 (1999).
- 19) Endo K., Yamanaka Y.: *Macromol. Chem. Phys.*, **202**, 201 (2001).
- 20) Endo K., Hatakeyama N.: *J. Polym. Sci. A*, **39**, 2798 (2001).
- 21) Endo K.: *Nippon Gomu Kyoukai*, **59**, 309 (2002).
- 22) Endo K., Hatakeyama N.: *Kobunshi Ronbunshu*, **70**, 69 (1997).
- 23) Endo K., Uchida Y., Matsuda Y.: *Macromol. Chem. Phys.*, **197**, 3515 (1996).