

Selective Chain Transfer Reactions in Metallocene Catalyzed Copolymerization of Ethylene with Allylbenzene

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Intensive research on the polymerization of olefins with metallocene catalysts has added a great number of details to the knowledge of the mechanism of olefin insertion/termination reactions and the relationship between catalyst symmetry and polymer microstructure. An understanding of the chain termination is an important issue because it is critical for the control of molecular weight and chain end structure of polymers. It is known that two kinds of chain transfer reactions, β -H elimination and chain transfer to aluminum, prevail in olefin polymerization with metallocene/MAO catalysts. However, only a few publications that describe the predominant occurrence of chain transfer to aluminum during olefin polymerization have appeared in the scientific literature.^{1–5} Generally, chain termination via alkyl chain transfer to aluminum is described as a minor chain termination process for the metallocene-catalyzed olefin polymerization.^{6–11} Recently we found that chain transfer to aluminum became a major chain transfer reaction when ethylene was copolymerized with allylbenzene.¹²

In this communication, we report the copolymerization behavior of ethylene and allylbenzene with several metallocene catalysts having different ligand structures where chain transfer mode depends on the catalysts' structures. The chain transfer behavior of ethylene–allylbenzene copolymerization was studied through analysis of the molecular weight and the chain end structures of the copolymers.

Ethylene was copolymerized with allylbenzene at 80 °C in the presence of 50×10^{-6} mol/L zirconocene catalysts and MAO (Al/Zr = 2000). Table 1 shows the results of catalytic activity, incorporation content of allylbenzene, and molecular weight of the copolymers. In the copolymerizations, the catalytic activity was increased with addition of allylbenzene compared to homopolymerization of ethylene. Comonomer effect on activity is frequently observed in olefin polymerization because of enhanced monomer diffusion into active sites or awakening of active site.^{13–15}

Incorporation content of the allylbenzene into the polymeric chain was determined by ¹H NMR spectroscopy. Table 1 showed that copolymer prepared with more hindered catalyst had a smaller amount of the allylbenzene unit. The incorporation of allylbenzene in the copolymer decreases in the following order: Cp₂-ZrCl₂ > (*n*-BuCp)₂ZrCl₂ > (2-MeInd)₂ZrCl₂ ≫ Cp*₂ZrCl₂. This effect can be explained in terms of accessibility of

the bulky comonomer to the active center, which is effected by the steric hindrance of the substituted ligands.¹³

It is well-known that the molecular weight of copolymers is influenced by the incorporation of the comonomer^{13–18} which facilitates chain transfer reactions, β -H elimination, or chain transfer to aluminum. As expected, the average molecular weight of the copolymers is smaller than that of ethylene homopolymer. Also the copolymers containing more allylbenzene units have lower molecular weights except for the copolymers made with (2-MeInd)₂ZrCl₂ (runs 6 and 11).¹⁹ To understand the chain transfer process in the ethylene–allylbenzene copolymerization, the copolymer solution was treated with dry air (oxidative workup) that converts aluminum terminal groups formed through chain transfer to aluminum to hydroxy groups. Then, the chain end structure of the copolymers was analyzed with NMR spectroscopy. Table 2 shows the data for the chain end structure of the copolymer obtained with oxidative workup. The percentages of chain transfer to aluminum were calculated from the hydroxy group contents in Table 2.

Under the polymerization condition investigated, significant amount of vinylidene end group was formed by β -H elimination in the copolymerization with Cp₂-ZrCl₂/MAO and (*n*-BuCp)₂ZrCl₂/MAO, while chain transfer to aluminum is highly preferred in the copolymerization with (2-MeInd)₂ZrCl₂/MAO and Cp*₂ZrCl₂/MAO.

The preference for β -H elimination in the copolymerization can be rationalized in terms of the chain conformation for β -agostic interaction, which is believed to stabilize the metal center.^{20–22} The typical polymer end groups, found in ethylene- α -olefin copolymer prepared by ordinary metallocene catalysts, are the vinylidene end group (Scheme 1g,h) generated by β -H elimination and the initial end group (methyl) (Scheme 1e,f) formed by insertion of monomer into the metal hydride.

When the chain transfer to aluminum occurs, the polymer end groups become the alkyl–aluminum group. Unambiguous evidence for the chain transfer to aluminum in the copolymerization can be obtained from oxidative workup.^{1,23} Oxidative workup of the aluminum-terminated polymer affords hydroxy-terminated polymers (Scheme 1c,d) of which ¹H and ¹³C NMR spectra are shown in Figure 1 and Figure 2.

The resonance at 3.5 ppm in the ¹H NMR spectra and at 65.4 ppm in the ¹³C NMR spectra are the peaks of the hydroxymethyl end group obtained from structure **3** in Scheme 1. Also, the resonance at 3.6 ppm in the ¹H NMR spectra and at 63.0 ppm in the ¹³C NMR spectra correspond to the hydroxymethyl end group obtained from structure **4** in Scheme 1. The two peaks at 4.7 ppm in the ¹H NMR spectra are corresponding to the vinylidene group formed by β -hydride elimination after allylbenzene insertion (Scheme 1g).

The vinylidene end group is detected predominantly in the case of using the catalysts having a less substituted Cp-type ligand, while the more hindered zirconocenes with substituted Cp-type ligands prefer chain transfer to aluminum to β -hydride elimination. These results suggest that the preference for β -hydride elimination vs aluminum transfer in metallocene-catalyzed

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Table 1. Results of Copolymerization of Ethylene and Allylbenzene with Various Zirconocenes/MAO Catalysts^a

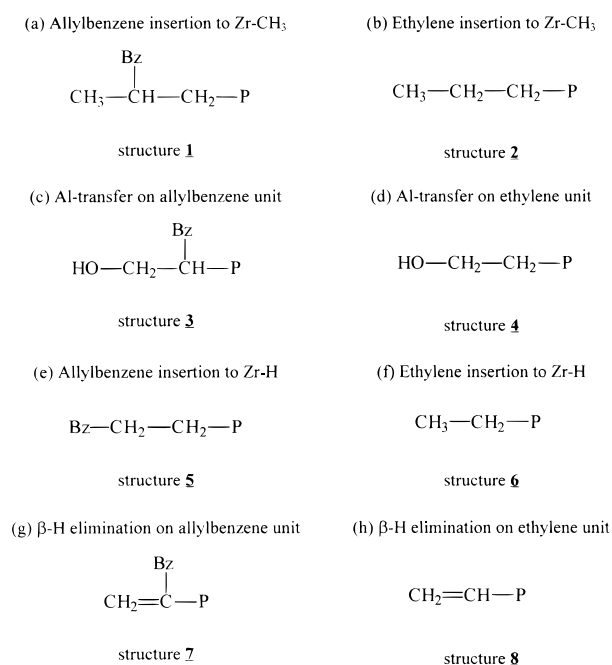
run	catalyst	allylbenzene concn (mol/L)	activity ^b	allylbenzene in copolymer ^c (mol %)	M_w	M_n	M_w/M_n
1	Cp ₂ ZrCl ₂	0.0	980	0.0	17000	6100	2.8
2	Cp ₂ ZrCl ₂	0.2	1370	3.2	9000	3900	2.3
3	(<i>n</i> -BuCp) ₂ ZrCl ₂	0.0	1190	0.0	8400	3000	2.8
4	(<i>n</i> -BuCp) ₂ ZrCl ₂	0.2	1330	3.2	6600	2800	2.4
5	(2-MeInd) ₂ ZrCl ₂	0.0	870	0.0	15000	5600	2.7
6	(2-MeInd) ₂ ZrCl ₂	0.2	1010	2.7	8700	3800	2.3
7	Cp* ₂ ZrCl ₂	0.0	260	0.0	4700	2000	2.4
8	Cp* ₂ ZrCl ₂	0.2	430	0.4	4600	2100	2.2

^a Polymerization conditions: amount of catalyst = 2.5×10^{-6} mol, Al/Zr = 2000, ethylene pressure = 1.2 bar, solvent = toluene, volume of total solution = 50 mL, temperature = 80 °C, and polymerization time = 1 h. ^b Activity = kilograms of polymer per mole of Zr per hour per 1 bar. ^c Calculated by ¹H NMR.

Table 2. Copolymerization Results and Chain End Structures of Ethylene–Allylbenzene Copolymers Obtained with Oxidative Workup^a

run	catalyst	allylbenzene in copolymer ^b (mol %)	M_w	M_w/M_n	terminal structure (mol %)				
					CH ₃ —CH ^c	CH ₃ —CH ₂ ^d	CH ₂ =C ^e	HO—CH ₂ CH ^f	HO—CH ₂ CH ₂ ^g
9	Cp ₂ ZrCl ₂	11.2	3100	1.6	21	25	38	12	4
10	(<i>n</i> -BuCp) ₂ ZrCl ₂	7.9	4000	1.8	28	24	20	19	8
11	(2-MeInd) ₂ ZrCl ₂	4.7	9000	2.4	37	27	2	28	7
12	Cp* ₂ ZrCl ₂	11.2	3500	1.8	8	58	0	0	34

^a Polymerization conditions: amount of catalyst = 2.5×10^{-6} mol, Al/Zr = 2000, ethylene pressure = 1.2 bar, allylbenzene = 1.0 mol/L (0.05 mol), solvent = toluene, volume of total solution = 50 mL, temperature = 80 °C, and polymerization time = 1 h. ^b Calculated by ¹H NMR. ^c Methyl end group obtained from structure **1** in Scheme 1. ^d Methyl end group obtained from structures **2** and **6** in Scheme 1. ^e Unsaturated end groups obtained from structures **7** and **8** in Scheme 1. ^f Hydroxymethyl end group obtained structure **3** in Scheme 1. ^g Hydroxymethyl end group obtained structure **4** in Scheme 1.

Scheme 1. Chain End Structures of Ethylene–Allylbenzene Copolymer: Bz = Benzyl Group; P = Polymer Chain

polymerization stems from the state of chain conformation for the β-agostic interaction. β-Hydride elimination is believed to occur through the β-agostic interaction.^{11,20,21}

Both β-hydride elimination and β-agostic interactions require the overlapping of a σ_{C-H} orbital with an empty d orbital of zirconium. The orbital overlapping demands that the first two chain carbons from the metal center and the β-hydrogen must be on the same equatorial plane containing the zirconium, between the two Cp-type ligands.^{2,20,22,24} When the propagating chain end

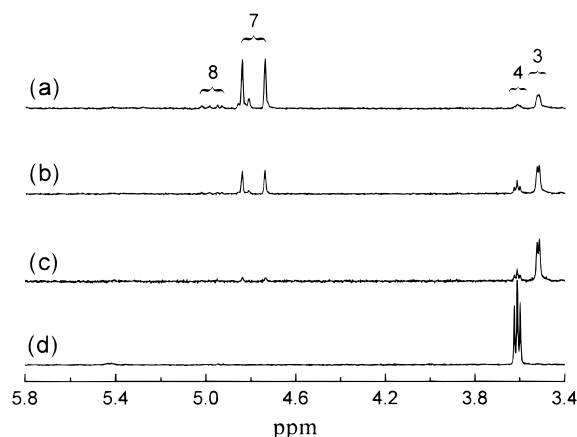


Figure 1. ¹H NMR spectra of ethylene–allylbenzene copolymers obtained with various zirconocenes/MAO catalysts: (a) Cp₂ZrCl₂ (run 9); (b) (*n*-BuCp)₂ZrCl₂ (run 10); (c) (2-MeInd)₂ZrCl₂ (run 11); (d) Cp*₂ZrCl₂ (run 12); (3) hydroxymethyl end group obtained from structure **3** in Scheme 1; (4) hydroxymethyl end group obtained from structure **4** in Scheme 1; (7) vinylidene end group obtained from structure **7** in Scheme 1; (8) vinyl end group obtained from structure **8** in Scheme 1.

is an allylbenzene unit, the β-agostic interaction at highly hindered zirconium center is sterically unfavorable because of the steric interaction between a bulky benzyl group on the β-carbon position and the substituted Cp-type ligand. Thus, the zirconium center without β-agostic interaction becomes electronically unstable and reactive to the aluminum compound as an alkylating agent.

Moreover, when the propagating chain end is an allylbenzene unit, subsequent insertion of a new monomer may be delayed because of the steric effect of the bulky benzyl group. Therefore, while β-H elimination is suppressed, chain transfer to aluminum is facilitated through free trimethylaluminum included in MAO solution which acts as an effective alkylating agent. As

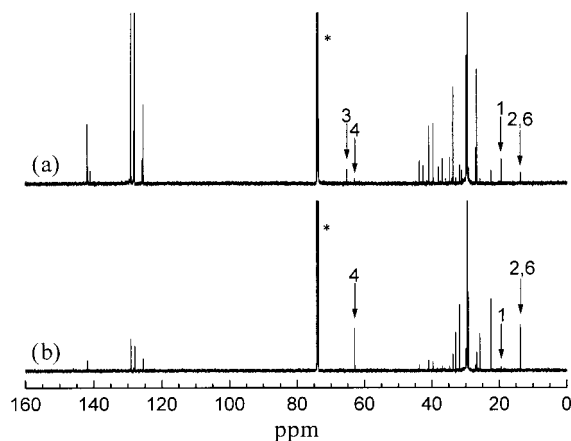


Figure 2. ^{13}C NMR spectra of ethylene-allylbenzene copolymer obtained with various zirconocenes/MAO catalysts: (a) $(2\text{-MeInd})_2\text{ZrCl}_2$ (run 11); (b) $\text{Cp}^*_2\text{ZrCl}_2$ (run 12); (1) methyl end group obtained from structure **1** in Scheme 1; (2) methyl end group obtained from structure **2** in Scheme 1; (3) hydroxymethyl end group obtained from structure **3** in Scheme 1; (4) hydroxymethyl end group obtained from structure **4** in Scheme 1; (6) methyl end group obtained from structure **6** in Scheme 1. The asterisk denotes a solvent peak.

an extreme case of hindered zirconocene, the copolymer obtained with $\text{Cp}^*_2\text{ZrCl}_2$ shows only one end group resulting from aluminum transfer after ethylene insertion as shown in Figure 1d (Scheme 1d).

In conclusion, depending on the ligand structure of the catalysts, different modes of chain transfer occurred selectively in ethylene-allylbenzene copolymerization. Chain transfer to aluminum is preferred rather than β -hydride elimination with highly substituted catalysts, while β -hydride elimination is preferred with less substituted catalysts. The selectivity for the chain transfer reaction is attributed to the feasibility of chain conformation for β -agostic interaction. Allylbenzene units incorporated at the polymer chain end enhanced the both chain transfer reactions of chain transfer to aluminum and β -hydride elimination, resulting in reduction of the molecular weight of the copolymers.

Experimental Section. Ethylene was deoxygenated and dried by passing it through columns of oxygen-scavenging catalyst and activated molecular sieves (4 Å). Zirconocene catalysts obtained from Strem were used as received. MAO was purchased from Akzo as a toluene solution (11.6 wt % aluminum, density 0.89 g/mL) and used without further purification. Allylbenzene was purchased from Aldrich and was vacuum distilled over calcium hydride. Toluene was distilled over calcium hydride and stored under nitrogen. All operations were carried out with standard Schlenk and vacuum techniques under a dry nitrogen atmosphere. Polymerization was carried out in a 100 mL jacketed glass reactor. Into the reactor dried at 80 °C in a vacuum was placed the proper amounts of toluene under an ethylene stream. The prescribed amounts of co-catalysts and allylbenzene were added to the reactor, and then the temperature was raised to 80 °C. After the toluene solution was saturated with ethylene, 2.5×10^{-6} mol of a zirconocene catalyst was injected at constant ethylene pressure (1.2 bar). All the polymerizations proceeded homogeneously (no precipitation) with ad-

equate stirring. Polymerization was terminated either by precipitation of the polymer with acidic methanol (acidic workup) or by bubbling dry air into the solution for 2 h followed by hydrolysis in acidic methanol (oxidative workup). The polymer obtained was washed with plenty of methanol and dried in a vacuum at 60 °C. All NMR spectra were run on a Bruker AMX500 spectrometer in tetrachloroethane- d_2 as solvent at 110 °C. Molecular weights and molecular weight distributions of the polymers were measured by means of gel permeation chromatography (Waters 150C) at 135 °C using 1,2,4-trichlorobenzene solvent and polystyrene standard.

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