Copolymerization of Ethylene with α-Olefins Over Supported Titanium–Magnesium Catalysts. II. Comonomer as a Chain Transfer Agent

Marina I. Nikolaeva, Mikhail A. Matsko, Tatiana B. Mikenas, Ludmila G. Echevskaya, Vladimir A. Zakharov

Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Science, Pr. Akademika Lavrentieva, 5 Novosibirsk 630090, Russia

ABSTRACT: The data on the effect of comonomer (propylene and 1-hexene) on molecular weight (M_w), molecular weight distribution (MWD), and content of terminal double bonds were obtained for ethylene/α-olefin copolymers produced over a supported titanium–magnesium catalyst (TMC) upon polymerization in the absence of hydrogen. The experimental data on the effect of comonomer concentration on M_w of polymers were used to calculate the ratios between the effective rate constants of chain transfer with monomer and the propagation rate constant. It was shown that the effective rate constant of chain transfer with monomers increases in the row of monomers: ethylene < 1-hexene < propylene. Meanwhile, the data on the effect of copolymers on content of terminal double bonds of various types demonstrate that different reactions of chain transfer with comonomer may simultaneously occur during copolymerization. It results in simultaneous formation of terminal vinylidene and *trans*-vinylene bonds. Therefore, the calculated rate constants of chain transfer with comonomer are complex values, which include the rate constants of chain transfer with comonomer occurring via different mechanisms. The data on MWD, short chain branching (SCB) and terminal double bonds content of different types were obtained by molecular weight fractionation of copolymers followed by the analysis of narrow fractions. The analysis of the data on MWDs of SCB and terminal double bonds shows that active sites of the TMC are considerably heterogeneous with respect to the rates of different chain transfer reactions with monomers. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2042–2049, 2012

Key words: Ziegler–Natta polymerization; copolymerization; kinetics (polym.); molecular weight distribution/molar mass; polyethylene

INTRODUCTION

A large number of polyethylene (PE) grades produced over catalysts with different compositions are ethylene/α-olefin. Rheological and physicomechanical properties of these polymers depend on their molecular-weight characteristics, comonomer content, and short chain branching (SCB) distribution. Many publications[1–12] were devoted to studying ethylene/α-olefin copolymerization on supported Ziegler catalysts (titanium–magnesium catalysts [TMCs]) and molecular structure of the resulting copolymers. It was shown[2,6–8,10–13] that the introduction of comonomer usually results in a decrease in molecular weight (M_w) of the polymer. Thus, comonomer acts as an additional chain transfer agent upon copolymerization. However, it should be noted that in most studies[6–8,10,11], the data on the effect of comonomer on M_w of polymers were obtained upon copolymerization in the presence of hydrogen, which is the most efficient chain transfer agent and predominantly determines molecular weight of the resulting polymers. To obtain the more detailed quantitative data on the reactions of chain transfer with α-olefins, it is reasonable to investigate the effect of α-olefin on M_w and molecular weight distribution (MWD) of polymers produced on supported Ziegler catalysts in the absence of hydrogen. A number of studies have been published[12,14] in which the data on M_w and MWD of ethylene/α-olefin copolymers obtained in the absence of hydrogen on Ziegler-type supported catalysts are presented. However, these studies do not contain the data on molecular-weight characteristics of the initial homopolymer, thus limiting the possibility of analyzing the reaction of chain transfer with α-olefin. It was found in Ref. 9 that the introduction of 1-octene upon ethylene/1-octene copolymerization on supported TMC with different composition of active component (TiCl₄ and (RO)TiCl₃) results in the increase in M_w of the resulting copolymers when

compared with the initial homopolymer. This result differs from those obtained in Refs. 2,6–8, and 10–13 at copolymerization of ethylene with propylene and 1-hexene.

In this work, we studied the influence of comonomers (propylene and 1-hexene) and their concentrations on M_w and MWD of polymers as well as nature and content of terminal double bonds in copolymers produced by copolymerization of ethylene with these comonomers on a supported TMC in the absence of hydrogen. The data on the effect of comonomer concentration on M_w were used to calculate the rate constants of chain transfer with propylene and 1-hexene. The comparative data on branching and terminal double bond distribution over molecular weight for ethylene/propylene (EP) and ethylene/1-hexene (EH) copolymers were obtained by molecular weight fractionation of copolymers followed by the analysis of narrow fractions.

EXPERIMENTAL

Catalyst TMC (2.6 wt % of Ti) was synthesized via a procedure described elsewhere[15] by supporting titanium tetrachloride on the support with the average particle size of 10 μm prepared by interaction of organomagnesium compound $Mg_3Ph_4Cl_2$ in dibutyl ether and PhCl with the mixture of $PhSiCl_3$ and $Si(OEt)_4$. The carrier of this catalyst contains ethoxy groups (16 wt %).

Polymerization was performed in a 0.85-L steel reactor, in heptane (250 mL), at constant ethylene pressure (2 bar), and polymerization temperature (80°C) for 1 hour; triethylaluminum ($[AlEt_3]$ = 2.6 mmol L^{-1}) was used as a cocatalyst, where catalyst concentration was 0.016–0.032 g L^{-1}.

At ethylene/1-hexene copolymerization, comonomer was introduced singly at the beginning of the experiment. The amount of the catalyst was selected so that the copolymer yield was limited to prevent the change of 1-hexene concentration over 15 wt %.

Ethylene/propylene copolymerization was carried out as follows. During copolymerization, the pressure was maintained by continuous introduction of a mixture of the gaseous monomers of definite molar ratio. In these experiments, the concentration of propylene tends first to increase, but after a certain period of time becomes constant. To ensure the constancy of comonomer concentration during the entire experiment, the high concentration of propylene being equal to one that typically established in the system during the experiment was taken as the initial concentration. The constancy of monomer concentrations during the copolymerization was controlled chromatographically.

Ethylene and propylene concentrations were calculated from their partial pressures with the Henry's law $C = K_H P$, where C is ethylene or propylene concentration (mol L^{-1}), K_H is Henry's constant (mol L^{-1} bar^{-1}), P is ethylene or propylene pressure (bar). The Henry's constants at 80°C for ethylene K_H = 0.071 M bar^{-1} and for propylene K_H = 0.28 M bar^{-1} according to Ref. 16.

MWD measurements were made on a high-temperature Waters 150°C gel permeation chromatograph combined with a Viscotek 100 differential viscometer, at 140°C in 1,2,4-trichlorobenzene at a flow rate of 1 mL min^{-1}. The polymers were analyzed using four TSK columns (GMHXL-HT, Tosoh Corp.). The instrument was calibrated using PE and polystyrene standards with narrow MWD.

Deconvolution of MWD curves was performed as described in Refs. 8,17. Copolymer fractionation into narrow fractions was carried out on a PolymerChar PREP mc2 fractionation instrument.[8] Next, the MWD and branching content were measured in each fraction by infrared (IR) spectroscopy on a Shimadzu FTIR 8400 spectrometer or by nuclear magnetic resonanace spectroscopy on a Bruker MSL-400 spectrometer.[18,19]

The number of double bonds was determined by IR spectroscopy on a Shimadzu FTIR 8400 S as described in Ref. 20,21. The content of vinyl, vinylidene, and *trans*-vinylene groups was estimated according to the intensity of 888, 909, and 965 cm^{-1} bands, respectively.

RESULTS AND DISCUSSION

In an earlier article,[22] we showed that PE with M_w < 1×10^6 g mol^{-1} can be produced upon ethylene polymerization at 80°C in the absence of hydrogen on TMC prepared according to Ref. 15, making it possible to reliably measure the MWD of the polymer by gel permission chromatography (GPC). Therefore, this catalytic system was used to study the influence of comonomer (propylene and 1-hexene) on M_w and MWD of copolymers produced in the absence of hydrogen.

Comonomer effect on the yield, M_w, MWD, and content of terminal double bonds in copolymers

Figure 1 shows the kinetic curves of ethylene/propylene and ethylene/1-hexene copolymerization compared with ethylene homopolymerization. The introduction of comonomer results in an abrupt increase in activity and change in the shape of kinetic curve as compared with ethylene homopolymerization. The shape of kinetic curve depends on nature and concentration of a comonomer. For ethylene/propylene copolymerization, the maximum activity is attained after 20 min of the reaction, and
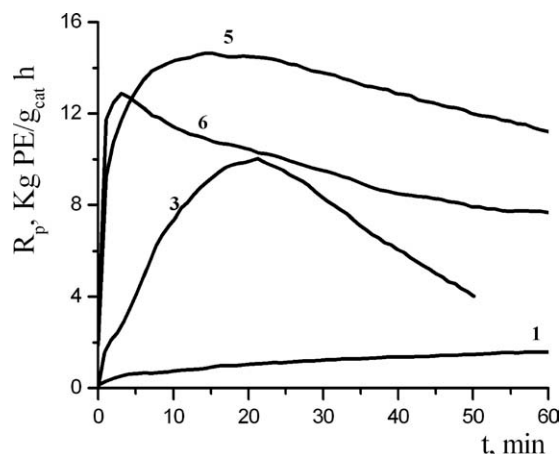
Figure 1 Kinetic curves of ethylene homopolymerization (curve 1) and copolymerization of ethylene with propylene (curve 3) and with 1-hexene (curves 5 and 6) over TMC in the absence of hydrogen. Curve numbers correspond to experiment numbers in Table I.

then decreases (Fig. 1, curve 3). Upon ethylene/1-hexene copolymerization, the maximum activity is attained after 3–10 min, and then decreases (Fig. 1, curves 5 and 6). The increase in activity upon copolymerization on Ti-based supported catalysts when compared with homopolymerization was noted earlier in numerous works.[1,6–10,23,24]

Table I summarizes the data on the effect of propylene and 1-hexene and their concentrations on the polymer yield, M_w, and MWD, as well as composition of the resulting copolymers and content of terminal double bonds. It can be seen that a considerable decrease in M_w of the resulting copolymers when compared with the homopolymer (experiments 1, 2, and 5) takes place after the introduction of a comonomer. With increasing comonomer concentration, the further decrease in M_w takes place (Table I, experiments 2, 3, 5, and 6). Figure 2(A,B) shows the MWD curves of PE and ethylene/propylene and ethylene/1-hexene copolymers produced at different concentrations of comonomers. On the MWD curve of PE (curve 1), there is a high molecular weight shoulder contributing to the MWD broadening and the high value $M_z = 3.7 \times 10^6$. The high molecular weight shoulder attenuates upon copolymerization (the M_z value decreases considerably); however, the share of the low molecular weight part increases simultaneously. The introduction of an α-olefin results in a small shift of the major peak of the MWD curves to the low molecular weight region in comparison with homopolymer. Further increase in α-olefin concentration has almost no effect on shape of the MWD curve. It should be noted that the copolymers with close comonomer content (2–2.3 mol %) have close M_w and MWD (experiments 2 and 6 in Table I).

TABLE I
Comonomer Effect on the M_w, MWD, Comonomer Content, and the Content of Terminal Double Bonds

| Experiment Number | Cα | Cα/C2[a] | Yield, kg PE/gCat | $M_n \times 10^{-3}$ | $M_w \times 10^{-3}$ | $M_z \times 10^{-3}$ | M_w/M_n | mol %[b] | Content of double bonds | | | | | |
| | | | | | | | | | CH₂=CHR | | CH₂=C<R¹R² | | R¹CH=CHR² | |
									Content per 1000 C	Content per polymer chain	Content per 1000 C	Content per polymer chain	Content per 1000 C	Content per polymer chain
1	–		1.2	76	690	3700	9.1	–	0.03	0.20	0.01	0.06	–	–
2	C₃H₆	0.18	4.7	50	420	1900	8.4	2.0	0.04	0.14	0.02	0.08	0.01	0.04
3		0.51	5.5	57	360	1300	6.3	4.9	0.06	0.23	0.04	0.14	0.03	0.10
4		8.0	1.7	23	190	1100	8.3	25.0	0.11	0.18	0.42	0.69	nd[c]	nd[c]
5	C₆H₁₂	2.3	12.5	59	540	2200	9.2	1.0	0.06	0.24	nd[d]	nd[d]	0.01	0.04
6		4.6	8.7	49	430	1900	8.8	2.3	0.07	0.24	nd[d]	nd[d]	0.02	0.07

[a] Molar ratio of a-olefin/ethylene upon polymerization.
[b] Comonomer (propylene or 1-hexene) content in copolymer.
[c] Not determined (the content of trans-vinylene bonds cannot be precisely determined because of overlapping bands at 937, 965, and 970 cm⁻¹).
[d] Not determined (the content of vinylidene bonds cannot be precisely determined because of overlapping bands at 888 and 895 cm⁻¹).
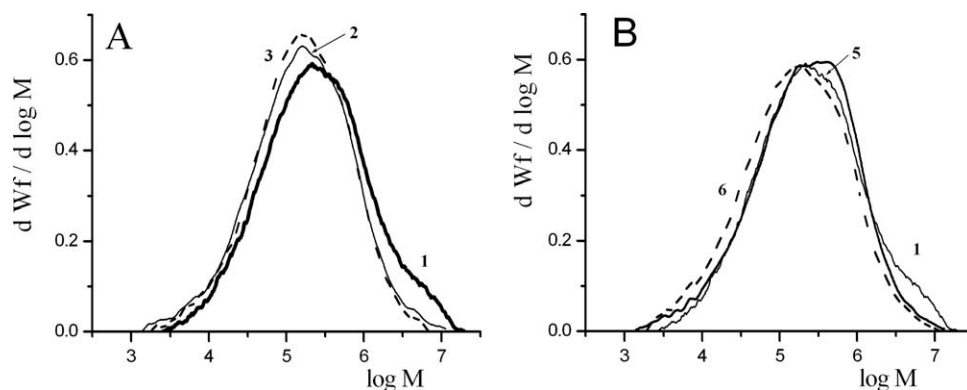
Figure 2 MWD curves of PE (curve 1) and ethylene/α-olefin copolymers. (A) Ethylene/propylene copolymers, curves 2 and 3; (B) ethylene/hexene-1 copolymers, curves 5 and 6; Curve numbers correspond to experiment numbers in Table I.

The additional information on the reactions of polymer chain transfer with comonomer can be obtained from the data on nature and content of double bonds in copolymers when compared with the homopolymer. Table I summarizes the data on the effect of comonomer composition and concentration on the number of terminal double bonds calculated per polymer chain in PE and ethylene/propylene and ethylene/1-hexene copolymers. The initial homopolymer predominantly contains vinyl groups that are formed in the reaction of chain transfer to ethylene.[22] The content of vinylidene groups is considerably lower when compared with that of vinyl groups. The presence of vinylidene groups is not typical for PE: they can be formed in side reactions, such as the reinsertion of ethylene macromonomer into the growing polymer chain followed by β-hydride chain transfer to monomer or β-hydride chain transfer to the transition metal atom of an active site (AS).[25] However, the contribution of these reactions is considerably lower when compared with the reaction of chain transfer to ethylene.

Figure 3 represents the IR spectra of PE (curve 1), ethylene/propylene copolymers (curves 2 and 4), and ethylene/1-hexene copolymer (curve 6). It can be seen that the band at 888 (corresponding to vinylidene groups) and bands at 909 and 992 cm^{-1} (corresponding to vinyl groups) are observed for PE (curve 1). The bands at 888, 909, and 992 cm^{-1} are observed for the ethylene/propylene copolymer (curve 2), as well. After the introduction of propylene, the band at 937 cm^{-1} (corresponding to the oscillations of isolated propylene links)[26] and the band at 965 cm^{-1} (corresponding to *trans*-vinylene groups) emerge. For the copolymer with high propylene content (curve 4), the band at 888, 909, 937, 965, and 970 cm^{-1} (corresponding to propylene units consisting of at least four links) is observed; the bands at 909, 937, 965, and 970 cm^{-1} overlapping. For this copolymer (curve 4), the contribution of the

band at 909 cm^{-1} can be estimated with an appreciably high accuracy, whereas it is impossible to isolate the band at 965 cm^{-1} against the background of intense bands at 937 and 970 cm^{-1}. A noticeable increase in content of terminal vinylidene groups is observed for ethylene/propylene copolymers; their content growing with increasing propylene concentration (experiments 2–4 in Table I). The effect of propylene on content of vinylidene groups is particularly noticeable for the copolymer produced at high propylene/ethylene molar ratio (C3/C2 = 8.0, experiment 4). In this sample, content of vinylidene groups is equal to 0.69 per polymer chain; the content of vinyl groups remains almost constant (0.18–0.20 per polymer chain). In the ethylene/1-hexene copolymer (curve 6), the bands at 888, 895 (resulting from pendular oscillations of methylene groups in butyl branching),[27] 909, 992, and 965 cm^{-1} are
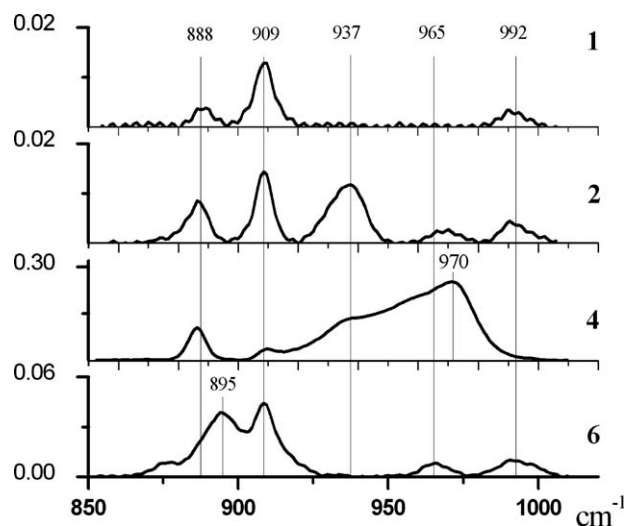

Figure 3 IR spectra of PE (experiment 1), ethylene/propylene copolymer (experiment 2 and 4) and ethylene/1-hexene copolymer (experiment 6). Curve numbers correspond to experiment numbers in Table I.

k_{tr}^{Al}, L$^{0.5}$ mol$^{-0.5}$ s^{-1}	K_{tr}^{H}, L mol^{-1} s^{-1}	k_{tr}^{Et}, L mol^{-1} s^{-1}	K_{tr}^{Pr}, L mol^{-1} s^{-1}	K_{tr}^{Hex}, L mol^{-1} s^{-1}
19[a]	180[a]	0.24[a]	2.0	0.5

[a] Values according to Ref. 22.

observed; the bands at 888 and 895 cm^{-1} are overlapping. The content of vinylidene groups cannot be accurately assessed because of strong overlapping of the bands at 888 and 895 cm^{-1} in ethylene/1-hexene copolymers. For ethylene/1-hexene copolymers (experiments 5 and 6 in Table I), the increase in content of *trans*-vinylene groups is observed with increasing 1-hexene concentration (experiments 5 and 6 in Table I); the content of vinyl groups remaining constant.

Four reactions of polymer chain transfer (transfer with a cocatalyst, with a monomer, β-hydride transfer, and transfer with hydrogen) are typically considered in polymerization of olefins on heterogeneous catalysts. In the article,[22] upon studying ethylene polymerization on the same catalyst as in this work, it was shown that vinyl groups in PE are formed as a result of the reaction of chain transfer to ethylene. The content of vinyl groups in this case depends on polymerization conditions (concentration of ethylene and cocatalyst) and may vary from 0.08 to 0.89 per polymer chain.[22]

It follows from the data summarized in Table I that the major contribution into the reactions of chain transfer with comonomer is made by the reactions yielding vinylidene and *trans*-vinylene groups (Scheme 1). The formation of these groups corresponds to the chain transfer reactions (2) and (3) with the participation of coordinated ethylene or α-olefin. In this case, Ti—CH₂—CH(R)-P terminal group formed after the 1,2-insertion of an α-olefin into the growing chain is involved into reaction (2), and Ti—CH(R) —CH₂P terminal group formed after the 2,1-insertion of an α-olefin into the growing chain is involved into reaction (3). It can be seen from the data summarized in Table I (experiments 2 and 3) that reactions (1), (2), and (3) can occur simultaneously upon copolymerization.

Calculation of the rate constants of chain transfer with propylene and 1-hexene

The ratio between the rate constant of polymer chain transfer with α-olefin to the rate constant of polymer propagation can be calculated using the experimental data on the effect of concentration of a comonomer (α-olefin) on the number average molecular weight (M_n) according to the expression (1):

$$\frac{1}{P_n} = \frac{\sum V_{tr}}{V_p} = \left(\frac{k_{tr}^{Et}}{k_p} + \frac{k_{tr}^{A1}[A1]^{0.5}}{k_p[C2]} \right) + \frac{k_{tr}^{C\alpha}[C\alpha]^n}{k_p[C2]} \quad (1)$$

where P_n is the degree of polymerization calculated using the M_n value; ΣV_{tr} is the sum of the chain transfer reaction rates; V_p is the propagation rate; k_p is the propagation rate constant; k_{tr}^{Et}, k_{tr}^{Al} are the reaction rate constants of chain transfer to ethylene and trialkylaluminum; $k_{tr}^{C\alpha}$ is the effective rate constant of chain transfer to α-olefin (reactions 2 and 3); n, the order of chain transfer reaction with respect to the comonomer; [C2], [Al], and [Cα] are concentrations of ethylene, trialkylaluminum, and α-olefin, respectively.

In our earlier article,[22] we showed that the reactions of chain transfer with triethylaluminum and ethylene take place upon ethylene polymerization on the TMC used in this work at 80°C in the absence of hydrogen and calculated the rate constants of these reactions.

The order of transfer reaction with respect to the monomer n was determined using the logarithmic form of expression (1); it turned out to be equal to 1. The $k_{tr}^{C\alpha}/k_p$ ratio for ethylene/propylene and ethylene/1-hexene copolymerization was calculated from the linear dependence of the degree of polymerization $1/P_n$ on the [Cα]/[C2] value. The ratios between the rate constant of chain transfer to comonomer and the propagation rate constant for propylene (k_{tr}^{Pr}) and 1-hexene (k_{tr}^{Hex}) are equal to 1.7×10^{-4} and 4.4×10^{-5}, respectively. It was found in Ref. 28 that k_p upon ethylene polymerization on TMC is equal to 1.2×10^4 L mol^{-1} s^{-1}. Taking this value into account, we calculated $k_{tr}^{C\alpha}$ values for propylene and 1-hexene. The calculated k_{tr}^{Pr} and k_{tr}^{Hex} values are listed in Table II, along with the constants of polymer chain transfer with triethylaluminum (k_{tr}^{Al}), hydrogen (k_{tr}^{H}), and ethylene (k_{tr}^{Et}), which were calculated in Ref. 22. It can be seen that the rate constants of chain transfer with ethylene and α-olefin increase in the row of monomers: ethylene < 1-hexene < propylene. The value k_{tr}^{Pr} is higher than k_{tr}^{Et} and k_{tr}^{Hex} by factors of 8.3 and 4, respectively.

However, it should be noted that the calculated values of $k_{tr}^{C\alpha}$ are of formalized character, since they represent the sum of different individual reactions into the process of chain transfer with an α-olefin (reactions (2) and (3)), as well as the reactions of insertion of α-olefins at Ti—CH₂CH₂P bond via the mechanism of 1,2- and 2,1-addition yielding structures (II) and (III) (Scheme 1, reactions 2 and 3) and reaction of coordination of monomers (ethylene and propylene, ethylene and 1-hexene) at active sites (II) and (III).
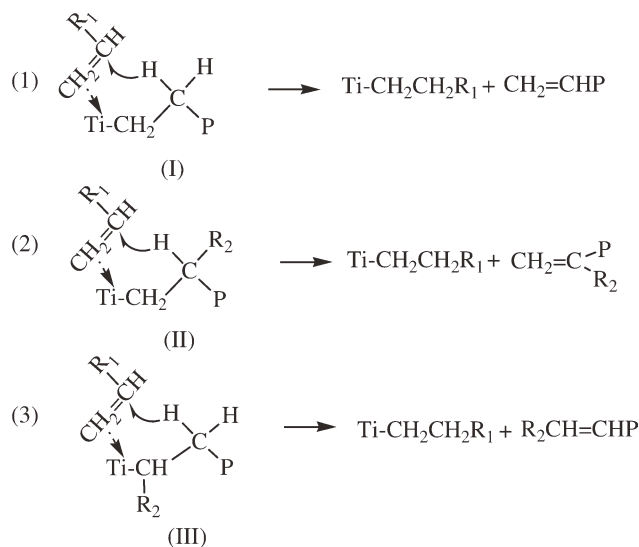
Scheme 1 Chain transfer reactions with a-olefon, where R_1·H, CH_3; R_2·CH_3 (for ethylene/propylene copolymerization); R_1. H, $CH_2CH_2CH_2CH_3$; R_2·$CH_2CH_2CH_2CH_3$ (for ethylene/1-hexene copolymerization).

Figure 4 MWD curves and SCB profiles of EP (solid) and EH (dash) copolymers with close comonomer content (experiment 2 and 6 in Table I).

Meanwhile, it follows from the data obtained that propylene and 1-hexene are more efficient chain transfer agents when compared with ethylene; and propylene is a considerably more efficient chain transfer agent when compared with 1-hexene. Moreover, the active sites of this catalyst are considerably heterogeneous with respect to the reaction of chain transfer with propylene and 1-hexene (as demonstrated below), which also makes a significant contribution to the averaged character of the calculated k_{tr}^{Pr} and k_{tr}^{Hex} values.

Heterogeneity of Active sites upon ethylene/α-olefin copolymerization

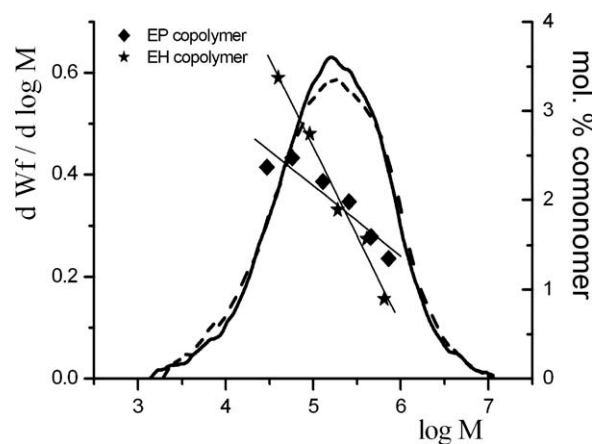Table III summarizes the results of deconvolution of the MWD curves for ethylene homopolymer and ethylene/propylene and ethylene/1-hexene copolymers into Flory components (experiments 1, 2, and 6 in Table I, Fig. 2). In experiments 2 and 6, copolymerization was performed at different $C\alpha/C2$ molar ratio (0.18 and 4.6, respectively). However, copolymers with similar M_w and M_w/M_n values and similar α-olefin content (2.0 and 2.3 mol %) were obtained in these experiments. The MWD curves of PE and copolymers are deconvoluted into 5 Flory components. The introduction of a comonomer results in a decrease in M_w of all Flory components and redistribution of contribution of individual Flory components: the contribution of low molecular weight components I and II decreases, whereas that of high molecular weight component IV rises.

Ethylene/propylene and ethylene/1-hexene copolymers (experiments 2 and 6 in Table I) were fractionated into narrow fractions followed by the analysis of these fractions to determine the content of SCB and content of terminal double bonds. Figure 4 represents the MWD curves obtained in these

TABLE III
Data on the Deconvolution of the MWD Curves into Flory Components [experiment numbers 1, 2, and 6 in Table 1 and Fig. 2(A,B)]

| | Homopolymer | | Ethylene/propylene copolymer | | Ethylene/1-hexene copolymer | |
| | 1[a] | | 2[a] | | 6[a] | |
Flory component	Percentage	$M_w \times 10^{-3}$	Percentage	$M_w \times 10^{-3}$	Percentage	$M_w \times 10^{-3}$
I	10.5	32	3.6	7	6.2	10
II	28.2	110	16.0	37	18.7	43
III	33.1	370	35.8	125	33.8	140
IV	19.1	1000	37.0	440	35.4	520
V	9.0	4300	11.0	1700	10.4	2000
Sum[b] $M_w \times 10^{-3}$	700		420		440	
M_w/M_n	9.0		7.6		9.7	

[a] Numbers correspond to experiment 1, 2, and 6 in Table 1.
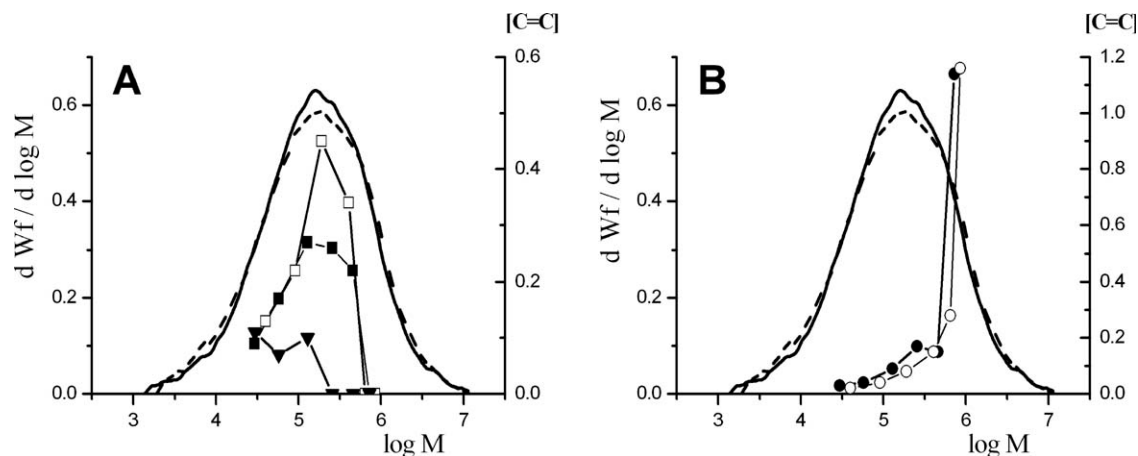[b] MWD of the sum of Flory components.

Figure 5 MWD curves and the distribution of double terminal bonds in EP (solid) and EH (dash) copolymers with close comonomer content (experiment 2 and 6 in Table I). (A) Vinyl double bonds per polymer chain. ■, EP copolymer; □, EH copolymer; ▲, vinylidene double bonds per polymer chain in EP copolymer. (B) *Trans*-vinylene double bonds per polymer chain. ●, EP copolymer; ○, EH copolymer.

experiments and the data of MWD of SCB for these copolymers. As can be seen, the SCB distribution in these copolymers differs dramatically. The higher homogeneity of comonomer distribution within the copolymer is typical for ethylene/propylene copolymer when compared with that for ethylene/1-hexene copolymer. The increased comonomer content in the low molecular weight part of the polymer is typical for the ethylene/1-hexene copolymer; the high molecular weight part of the polymer having lower content of the comonomer.

Figure 5 represents the data on MWD of terminal double bonds for ethylene/propylene and ethylene/1-hexene copolymers (experiments 2 and 6 in Table I). Vinyl bonds are present in low and medium molecular weight fractions of the polymer ($M_w < 5 \times 10^5$), whereas vinylidene terminal groups are present only in the fractions with lower molecular weight ($M_w < 2 \times 10^5$) [Fig. 5(A)]. There are no vinyl and vinylidene bonds in high molecular weight fractions with $M_w > 5 \times 10^5$. The distribution of *trans*-vinylene groups differs dramatically from that of vinyl and vinylidene groups [Fig. 5(B)]. The fractions with $M_w < 5 \times 10^5$ contain almost no *trans*-vinylene groups; however, their content increases abruptly with M_w rising to 5×10^5 (the high molecular weight fraction with M_w of 1×10^6 contains approximately one *trans*-vinylene group per polymer chain). Since the nature of terminal double bonds that are formed in the reaction of chain transfer with α-olefin is predominantly defined by the structure of a terminal group bound to the titanium atom in the AS (I, II, and III, Scheme 1), a conclusion can be drawn that 1,2-insertion of a comonomer (formation of structure II) is dominating at active sites producing the polymer with $M_w > 5 \times 10^5$. As a result, the transfer reaction (2) (Scheme 1) takes place predomi-

nantly at the active sites producing the polymer with $M_w < 2 \times 10^5$, whereas the transfer reaction (3) predominantly takes place at the active sites producing the polymer with $M_w > 5 \times 10^5$.

CONCLUSIONS

The data on the effect of nature and concentration of a comonomer (propylene and 1-hexene) on M_w and MWD of copolymers and on the content of terminal double bonds for ethylene/α-olefin copolymers produced on a supported TMC upon polymerization in the absence of hydrogen were obtained in this work. The results obtained allow assessing the role of a comonomer as an efficient chain transfer agent that has a considerable effect on M_w and MWD of the polymer produced upon ethylene/α-olefin copolymerization. The introduction of a comonomer results in a considerable decrease in M_w (Table I); the attenuation of the high molecular weight shoulder that is present on the MWD curve of the initial homopolymer being observed on the MWD curves of the copolymers (Fig. 2). The results of deconvolution of the MWD curve of ethylene/propylene copolymer into Flory components (Table III) show that the decrease in M_w of the copolymer when compared with the homopolymer takes place due to the reduction of M_w produced at each active site.

Based on the data on the effect that comonomers have on nature and content of terminal double bonds (vinyl, vinylidene, and *trans*-vinylene), the simultaneous occurrence of the reactions of chain transfer with comonomer with the participation of Ti—CH₂—CH(R)-P terminal group that is formed after 1,2-insertion of an α-olefin into the growing chain

(Scheme 1, reaction 2) and Ti—CH(R) —CH$_2$P terminal group that is formed after the 2,1-insertion of an α-olefin into the growing polymer chain was demonstrated.

The effective reaction rate constants of chain transfer with propylene (k_{tr}^{Pr}) and 1-hexene (k_{tr}^{Hex}) were calculated using the data on the effect of propylene and 1-hexene concentrations on M_w of copolymers (Table II). The rate constant of chain transfer with monomers was found to increase in the monomer row: ethylene < 1-hexene < propylene. However, it should be noted that the calculated constants of chain transfer with propylene and 1-hexene are formal values depending on the reactions of chain transfer that occur simultaneously in accordance with Scheme 1 and on the heterogeneity of active sites in the reaction of chain transfer with α-olefin that was revealed by the analysis of distribution of vinyl, vinylidene, and *trans*-vinylene bonds in copolymers.

The data on the MWD of SCB and terminal bonds were obtained by fractionation of copolymers on MM and analysis of narrow fractions (Figs. 4 and 5). The higher heterogeneity of ethylene/1-hexene copolymers when compared with ethylene/propylene copolymers was demonstrated. It was also shown that the distribution of vinyl, vinylidene, and *trans*-vinylene groups in the copolymer differs considerably. Vinyl bonds are present in low and medium molecular weight fractions of the polymer, whereas vinylidene terminal bonds are present only in low molecular weight fractions. In high molecular weight fractions, no vinyl and vinylidene groups are found. On the contrary, there are almost no *trans*-vinylene groups in low and medium molecular weight fractions; however, their content increases abruptly in the polymer part with high molecular weight.

It follows from the data presented that active sites of TMC have different character of heterogeneity relative to the rate constants of chain transfer with α-olefins and the rate constants of α-olefin insertion into the polymer chain. The active sites, on which the polymer with $M_w > 2 \times 10^5$ is formed, have an increased reactivity in the reactions of polymer chain transfer with α-olefin (Scheme 1, reaction 3), simultaneously having a very low reactivity in the reaction of α-olefin insertion into the growing polymer chain. Reaction 2 (Scheme 1) predominantly takes place at the active sites producing the polymer with $M_w < 5 \times 10^5$; simultaneously, these active sites are characterized by a high reactivity in the reaction of α-olefin insertion into the growing polymer chain.

References

1. Finogenova, L. T.; Zakharov, V. A.; Buniyatzade, A. A.; Bukatov, G. D.; Plaksunov, T. K. Vysokomol Soedin A 1980, 22, 404.
2. Kissin, Y. V.; Mink, R. I.; Nowlin, T. E. J Polym Sci A: Polym Chem 1999, 37, 4255.
3. Zhang, M. Q.; Lynch, D. T.; Wanke, S. E. J Appl Polym Sci 2000, 75, 960.
4. Silva Filho, A. A.; Soares, J. B. P.; Galland, G. B. Macromol Chem Phys 2000, 201, 1226.
5. Kissin, Y. V.; Mirabella, F. M.; Meverden, C. C. J Polym Sci A: Polym Chem 2005, 43, 4351.
6. Echevskaya, L. G.; Matsko, M. A.; Mikenas, T. B.; Nikitin, V. E.; Zakharov, V. A. J Appl Polym Sci 2006, 102, 5436.
7. Zakharov, V.; Echevskaya, L.; Mikenas, T.; Matsko, M.; Tregubov, A.; Vanina, M.; Nikolaeva, M. Chin J Polym Sci 2008, 26, 553.
8. Matsko, M. A.; Echevskaya, L. G.; Zakharov, V. A.; Nikolaeva, M. I.; Mikenas, T. B.; Vanina, M. P. Macromol Symp 2009, 282, 157.
9. Kong, Y. A.; Yi, J. J.; Dou, X. L.; Liu, W. J.; Huang, Q. G.; Gao, K. J.; Yang, W. T. Polymer 2010, 51, 3859.
10. Garoff, T.; Mannonen, L.; Vaananen, M.; Eriksson, V.; Kallio, K.; Waldvogel, P. J Appl Polym Sci 2010, 115, 826.
11. Huang, J. C. K.; Lacombe, Y.; Lynch, D. T.; Wanke, S. E. Ind Eng Chem Res 1997, 36, 1136.
12. Chu, K. J.; Soares, J. B. P.; Penlidis, A.; Ihm, S. K. Eur Polym J 2000, 36, 3.
13. Kim, J. H.; Jeong, Y. T.; Woo, S. I. J Polym Sci A: Polym Chem 1994, 32, 2979.
14. Perin, S. G. M.; Severn, J. R.; Koning, C. E.; Chadwick, J. C. Macromol Chem Phys 2006, 207, 50.
15. Mikenas, T. B.; Nikitin, V. E.; Zakharov, V. A. 2005 Rus. Pat. 2,257,264.
16. Kissin, Y. V. J Polym Sci A: Polym Chem 2003, 41, 1745.
17. Nikolaeva, M. I.; Mikenas, T. B.; Matsko, M. A.; Echevskaya, L. G.; Zakharov, V. A. J Appl Polym Sci 2010, 115, 2432.
18. Randall, J. C. Polymer Sequence determination; Academic: New York, 1977.
19. Echevskaya, L. G.; Zakharov, V. A.; Golovin, A. V.; Mikenas, T. B. Macromol Chem Phys 1999, 200, 1434.
20. Goldenberg, A. L.; Lubetskii, S. G. Vysokomol Soedin 1963, 5, 905.
21. Kashiwa, N.; Tsutsui, T.; Toyota, A. Polym Bull 1985, 13, 511.
22. Nikolaeva, M. I.; Mikenas, T. B.; Matsko, M. A.; Echevskaya, L. G.; Zakharov, V. A. J Appl Polym Sci 2011, 122, 3092.
23. Kissin, Y. V.; Mink, R. I.; Nowlin, T. E.; Brandolini, A. J. J Polym Sci A: Polym Chem 1999, 37, 4281.
24. Kissin, Y. V.; Mink, R. I.; Nowlin, T. E.; Brandolini, A. J. Top Catal 1999, 7, 69.
25. Bialek, M. J Polym Sci A: Polym Chem 2010, 48, 3209.
26. Tosi, C.; Valvassori, A.; Ciampelli, F. Europ Polym J 1968, 4, 107.
27. Lamonte, J. Analyt Chem 1962, 34, 129.
28. Zakharov, V. A.; Bukatov, G. D.; Barabanov, A. A. Macromol Symp 2004, 213, 19.