Study of the Compositional Heterogeneity of Ethylene/1–Hexene Copolymers Produced over Supported Catalysts of Different Composition

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ABSTRACT: Separation into narrow MWD fractions (liquid–liquid fractionation) and preparative TREF (temperature rising elution fractionation) with subsequent analysis of fractions by GPC, FTIR, and ^{13}C NMR spectroscopy were used to study the comonomer distribution of ethylene/1–hexene copolymers produced over highly active supported titanium- and vanadium-magnesium catalysts (TMC and VMC) and a supported zirconocene catalyst. These catalysts produce PE with different MWD: M_w/M_n values vary from 2.9 for zirconocene catalyst, 4.0 for TMC, and 15 for VMC. 1-Hexene increases polydispersity to 25 for copolymer produced over VMC and hardly affects MWD of the copolymer produced over TMC and zirconocene catalysts. The most broad short chain branching distribution (SCBD) was found for ethylene/1–hexene copolymers produced over TMC. VMC and supported zirconocene catalyst produce copolymers with uniform profile of SCB content vs. molecular weight in spite of great differences in M_w/M_n values (22 and 2.5 respectively). TREF data showed that majority of copolymer produced over supported zirconocene catalyst was eluted at 70–90°C (about 85 wt %). In the case of VMC copolymer's fractions were eluted in the broad temperature interval (40–100°C). Accordingly, TREF data indicate a more homogeneous SCBD in copolymer, produced over supported zirconocene catalyst. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: Ziegler-Natta polymerization; copolymers; fractionation of polymers; molecular weight distribution/molar; branched

INTRODUCTION

Ethylene/α-olefin copolymers produced over supported Ziegler-Natta catalysts are widely used in industry. Their physicomechanical and rheological properties are determined by the molecular and supramolecular structure, which depends on molecular weight characteristics, comonomer content, and homogeneity of branching distribution for polymer chains with different molecular weight (compositional heterogeneity). Comonomer content and distribution strongly affect such features of copolymers as density, processability, thermo-oxidative stability, stress crack resistance, impact strength, hot tack, heat seal, hexane extractable, etc.[1–6] Besides, data on MWD and comonomer distribution in ethylene/α-olefin copolymers make it possible to analyze the mechanism of polymerization reaction, in particular, the heterogeneity of active sites in the systems under study. Numerous works are devoted to studying the branch distribution in copolymers produced over catalysts of various compositions. Reported data show that copolymers produced over supported titanium-magnesium catalysts are compositionally heterogeneous: comonomer units are concentrated mainly in the low molecular weight part of the polymer.[7–11] To obtain copolymers with a more homogeneous composition on the Ziegler-type catalysts, we have used the vanadium-magnesium catalytic systems.[12,13] Preliminary data obtained in our experiments with copolymers having low content of 1-hexene are reported in Ref. 13, indicating that copolymers produced over VMC are much more homogeneous in composition as compared to those produced over TMC.

In the present work, a wide set of ethylene/1–hexene copolymers of various composition produced over TMC, VMC, and a supported zirconocene catalyst $SiO_2(MAO)/Me_2Si(Ind)_2ZrCl_2$ was synthesized and examined. These copolymers were fractionated into narrow fractions according to their molecular weight and comonomer content. The narrow fractions were investigated by means of GPC, FTIR, and ^{13}C NMR spectroscopy. The data obtained allowed us to reveal the effect of supported catalysts composition on the parameters of comonomer distribution in a broad range of compositions.

TABLE I
Polymerization Conditions and Characteristics of PE Samples and Ethylene/1–Hexene Copolymers Under Study

Catalyst	Catalyst activity, kg PE/g mt × h × MPa	[C6]/[C2]^a	Polymer no.	CH_3/1000 C	M_w, × 10^{-3}	M_w/M_n	M_z/M_w	T_m, °C	X_c, %	r_1 ^{e}
TMC^b	330	–	1	–	330	4.9	2.8	138.1	68	100
	1700	2.3	2	10	180	4.7	2.8	127.7	39	
	2000	4.6	3	20	150	4.0	2.8	126.1	33	
VMC^c	240	–	4	1.8	540	15	3.3	135.8	69	24
	450	0.65	5	11	300	25	5.3	126.7	45	
	350	1.2	6	19	215	22	6.3	124.2	36	
SiO$_2$(MAO)/	1100	–	7	–	150	2.9	2.5	135.8	72	11
Me$_2$Si(Ind)$_2$ZrCl$_2$^{d}	2200	0.23	8	10	110	2.4	2.4	119.0	42	
	860	0.40	9	16	110	2.8	2.4	114.1	26	

^{a} Concentration ratio of 1-hexene and ethylene in heptane.
^{b} Polymerization at ethylene pressure 0.2 MPa and $[H_2]/[C_2H_4] = 0.13$ in the gas phase.
^{c} Polymerization at ethylene pressure 0.4 MPa and $[H_2]/[C_2H_4] = 0.05$ in the gas phase.
^{d} Polymerization at ethylene pressure 0.5 MPa.
^{e} Comonomer reactivity ratios.

EXPERIMENTAL

Catalyst preparation

The titanium-magnesium (3.5 wt % Ti, TMC) and vanadium-magnesium (3.8 wt % V, VMC) catalysts were synthesized by supporting of $TiCl_4$[14] or VCl_4[15] on a highly dispersed magnesium chloride with the average particle size of 5 μm and a narrow particle size distribution.

The supported zirconocene catalyst SiO$_2$(MAO)/Me$_2$Si(Ind)$_2$ZrCl$_2$ was prepared by treatment of SiO$_2$(MAO) support with toluene solution of Me$_2$Si(Ind)$_2$ZrCl$_2$. The resulting catalyst contains 15 wt % Al and 0.15 wt % Zr.

Ethylene polymerization

Ethylene polymerization and copolymerization of ethylene with 1-hexene over TMC and VMC were performed in a 0.8-L steel autoclave in heptane at 80°C with hydrogen as a chain transfer agent. The catalyst concentration was 0.02–0.03 g/L; triisobutylaluminum (TIBA) with a concentration of 4.5 mmol/L was used as a cocatalyst.

Copolymerization of ethylene with 1-hexene over zirconocene catalyst was carried out in a 0.5-L steel autoclave in heptane at 80°C, ethylene pressure of 0.5 MPa in the presence of TIBA. The catalyst concentration was 0.33 g/L, the concentration of TIBA 3.5 mmol/L.

Polymerization time and yield of copolymers were chosen so as to retain a decrease in 1-hexene concentration within 10 wt %. Data on polymerization conditions and characteristics of the resulting polymers are presented in Table I.

MWD measurements

MWD measurements were made on a high-temperature Waters 150C 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. The polymers were analyzed using four TSK columns (GMHXL-HT, Tosoh Corp.). The instrument was calibrated using polyethylene and polystyrene standards with narrow MWD.

The melting temperature and crystallinity

The melting temperature (T_m) and crystallinity (X_c) were determined on a DSC 204 F1 (Netzsch) instrument according to ASTM D3418-82 and ASTM D3417-83 procedures in an argon atmosphere. The instrument was calibrated in compliance with,[16,17] against reference samples, indium (Aldrich), and zinc (Aldrich). A sample was examined using the melting—crystallization—melting program in the temperature range of 25–180°C at a rate of 10°C/min. The melting temperature and enthalpy (ΔH) were found from data of the second melting.

Separation of polymers

Separation of polymers into fractions with narrow MWD was performed using a PolymerChar fractionation station PREP mc^2. One gram of a sample was dissolved in definite volume of xylene for 2 h, then a calculated amount of 2-(2-butoxyethoxy)-ethanol was added in a polymer solution to precipitate a part of polymer. The total volume of liquid (xylene and 2-(2-butoxyethoxy)-ethanol) was always 180 mL. Hot solution of the polymer was filtered into collecting flask. The precipitated polymer was dissolved in a new portion of xylene; the precipitation-dissolution procedure was repeated to obtain 5–6 fractions with a narrow MWD. The last fraction was washed with pure xylene.
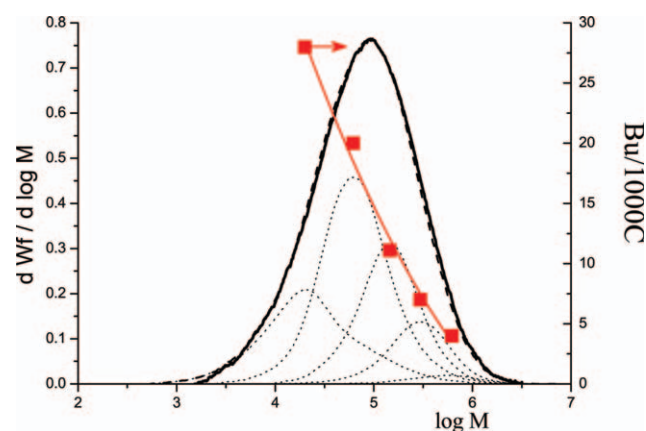
Separation of polymers into fractions with narrow composition (preparative TREF method) was
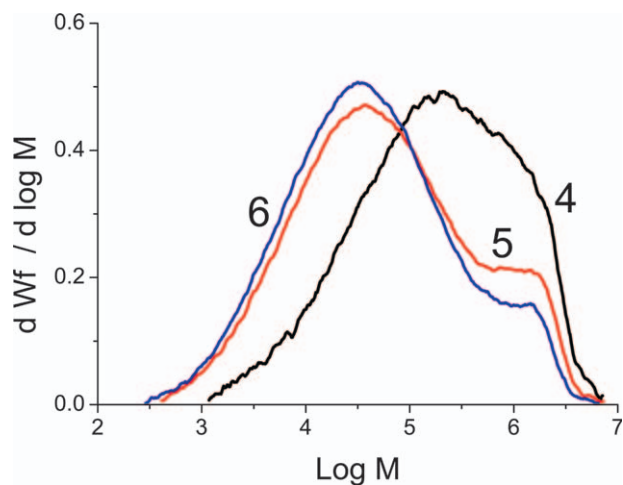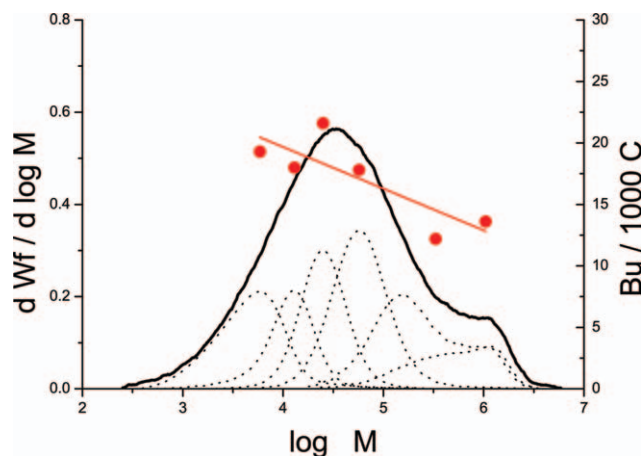
Figure 1 GPC curves for polymers produced over VMC. Numbering of experiments corresponds to Table I. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3 GPC curves for initial copolymer (solid line), individual fractions (dotted curves), and a profile of branching distribution (●) in copolymer produced over VMC (exp. 6, Table I). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

performed using an automated PolymerChar fractionation station PREP mc². One gram of a sample was dissolved in 200 mL of xylene at 130°C for 2 h. Then the temperature was decreased to 95°C and solution was held during 45 min for stabilization. Then the solution temperature was slowly decreased to 30°C at a continuous cooling rate of 0.1°C/min (crystallization step). The temperature was then increase to 40°C at the rate of 20°C/h and polymer solution was filtered into a collecting flask.

The precipitated polymer was dissolved again in a new portion of xylene at the next temperature step (50°C). The temperature was then increased discontinuously up to 110°C at the rate of 20°C/h in 10°C steps. This temperature is sufficient for

complete removal of polymers from fractionation vessels. Fractions were precipitated with an excess of acetone; filtered and dried at vacuum at 60°C to obtain a constant weight.

Comonomer content in copolymers and in fractions was determined by FTIR and ^{13}C NMR spectroscopy in accordance with[18,19] using an IR spectrometer Shimadzu FTIR 8400 S and an NMR spectrometer Bruker MSL-400. When comonomer content was estimated by IR spectroscopy, the content of terminal methyl groups was subtracted from the total amount of methyl groups. The content of the terminal methyl groups was calculated from the M_n values determined by GPC.
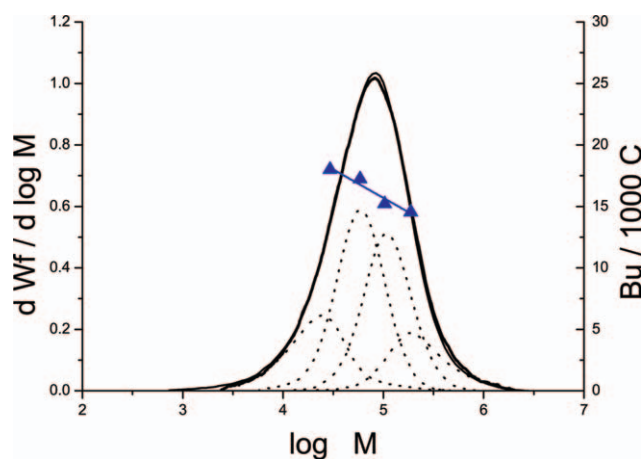

Figure 2 GPC curves for initial copolymer (solid line), individual fractions (dotted curves), and a profile of branching distribution (■) in copolymer produced over TMC (exp. 3, Table I). [Color figure can be viewed in the

Figure 4 GPC curves for initial copolymer (solid line), individual fractions (dotted curves), and a profile of branching distribution (▲) in copolymer produced over zirconocene catalyst (exp. 9, Table I). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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TABLE II
Data on Separate Fractions of Ethylene/1–Hexene Copolymer Produced Over TMC (exp. 3, Table I)

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Polymer	Content of 2-(2-butoxyethoxy) ethanol in a mixture, %	Fraction amount, %	$M_{peak} \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	CH$_3$/1000 C	Butyl/1000 C[a]
Initial polymer	–	–		148	4.0	20.0	19.2
F1	57	23.1	20	53	4.1	–	28.2
F2	43	40.3	62	96	2.2	17.7	17.1
F3	40	24.3	145	186	1.9	11.1	11.1
F4	38	10.7	295	350	1.9	7.0	7.0
F5	0	1.6	617	620	1.9	4.0	4.0
Sum of fractions	–	100		140	4.2		

[a] Content of butyl branches for fraction F1 was determined by ^{13}C NMR spectroscopy; in the other cases, by FTIR spectroscopy.

RESULTS AND DISCUSSION

Table I lists data on the catalyst activity and characteristics of homo- and copolymers of different composition produced over TMC (samples 1–3), VMC (samples 4–6), and supported zirconocene catalyst (samples 7–9). One may see that the catalysts under study are highly active toward ethylene polymerization and copolymerization of ethylene with 1-hexene.

Earlier we have demonstrated a higher copolymerization ability of VMC (lower values of comonomer reactivity ratio) in comparison with TMC[20,21] and a higher sensitivity of VMC to hydrogen.[22,23] In this connection, copolymers with the $1.5*10^5$–$3*10^5$ molecular weight and 10–20 CH$_3$/1000C branching can be obtained over VMC at lower [C$_6$H$_{12}$]/[C$_2$H$_4$] and [H$_2$]/[C$_2$H$_4$] ratios under polymerization conditions (Table I).

Data on the MWD for polymers under study are presented in Table I. It is seen that the introduction of 1-hexene and further increase of its content in the case of TMC and VMC decrease the molecular weight polymers being produced. Contrary to TMC, VMC allows obtaining polyethylene with a broad and bimodal MWD (Fig. 1). Upon introduction of 1-hexene and further increase of its content in copolymers produced over VMC, the main peak on the MWD curve is shifted to the low molecular weight region, whereas the position of high molecular weight shoulder shows only a slight change. Therewith, the shape of the MWD curves alters toward a more pronounced bimodality. As a result, the molecular weight decreases and MWD broadens considerably (Table I).

For comparison, Table I (exp. 7–9) lists the characteristics of polymers produced over the supported zirconocene catalyst. They have a narrow MWD as compared to copolymers produced over TMC and VMC catalysts. It should be noted also that in order to obtain copolymers with close molecular weights and compositions over zirconocene catalyst, polymerization was performed without hydrogen and at lower [C$_6$H$_{12}$]/[C$_2$H$_4$] ratios than in the case of TMC and VMC.

Table I presents also the DSC data for polymer samples being examined. The polymer melting curves are characterized by a single peak, its position shifting to the low-temperature region upon introduction of comonomer and further increase of its content. Crystallinity decreases in the same series. Copolymers produced over the zirconocene catalyst have lower melting temperatures and crystallinity in comparison with copolymers of a similar composition

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TABLE III
Data on Fractionation of Ethylene/1–Hexene Copolymer Produced Over VMC (exp. 6, Table I)

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Polymer	Content of 2-(2-butoxyethoxy)-ethanol in a mixture, %	Fraction amount, %	$M_{peak} \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	CH$_3$/1000 C	Butyl/1000 C[a]
Initial polymer	–	100		215	22	19.0	16.2
F1	70	17.1	5.9	6.7	1.6		19.6
F2	57	12.1	13	15	1.4		18
F3	49	17.1	25	30	1.3	22.9	21.6
F4	43	23.6	57	90	1.6	18.4	17.8
F5	40	20.4	162	670	4.2	12.4	12.2
F6	0	9.7	1050	1450	5.4	13.7	13.6
Sum of fractions	–	100	–	230	21	–	–

[a] Content of butyl branches for fractions F1 and F2 was determined by ^{13}C NMR spectroscopy; in the other cases, by FTIR spectroscopy.

TABLE IV
Data on Fractionation of Ethylene/1–Hexene Copolymer Produced Over Supported Zirconocene Catalyst (exp. 9, Table I)

Polymer	Content of 2-(2-butoxyethoxy)-ethanol in a mixture, %	Fraction amount, %	$M_{peak} \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	$CH_3/1000$ C	Butyl/1000 C[a]
Initial polymer	–	–	–	110	2.5	16	15.4
F1	51	19.1	24.7	30	2.3	–	18
F2	43	36.3	59	68	1.4	17.8	17.2
F3	41	31.2	110	130	1.4	15.5	15.2
F4	0	13.4	188	290	1.7	14.7	14.5
Sum of fractions	–	100	–	110	2.9		

[a] Content of butyl branches for fraction F1 was determined by ^{13}C NMR spectroscopy; in the other cases, by FTIR spectroscopy.

produced over TMC and VMC, which corresponds to the literature data.[24]

To determine the branching distribution, copolymers were separated into fractions with narrow MWD using the fractionation station. Then we measured the MWD and the branching content in each fraction by FTIR or ^{13}C NMR spectroscopy. The separation took into account MWD of initial copolymers. Six, five, and four fractions, respectively, were obtained for copolymers synthesized over VMC, TMC, and zirconocene catalyst. A ratio of 2-(2-butoxyethoxy)-ethanol to xylene was the main variable parameter. Note that branching of low molecular weight fractions of copolymers under study, where the content of terminal groups is especially high, was determined by ^{13}C NMR spectroscopy in order to separate the butyl branching, caused by the presence of hexene units in a polymer chain, from the end methyl groups. Tables II–IV show the fractionation results for copolymers produced over catalysts of various composition: the separation conditions for each fraction (amount of 2-(2-butoxyethoxy)-etha-

nol), the amount of a fraction in the total polymer, the MWD parameters of fraction and branching, and the calculated MWD for the sum of fractions taking into account their amounts. Tables II–IV indicate that polymers were separated into fractions with a rather narrow MWD, and the sum of the fractions agrees well with the MWD of initial copolymers.

The fractionation results were used to construct a profile of branching distribution in copolymers as a function of molecular weight (Figs. 2–4). Figures 2–4 present the MWD curves for copolymer fractions from Tables II–IV with regard to the contribution of each fraction to the total polymer. The branching content of each fraction is marked at the peak points on the MWD curves of appropriate fractions to construct a profile of comonomer distribution versus molecular weight. The profile is based only on butyl branching caused by the presence of comonomer units in copolymer chain.

As seen from Table II and Figure 2, ethylene/1–hexene copolymer produced over TMC has a very heterogeneous composition: the greatest amount of
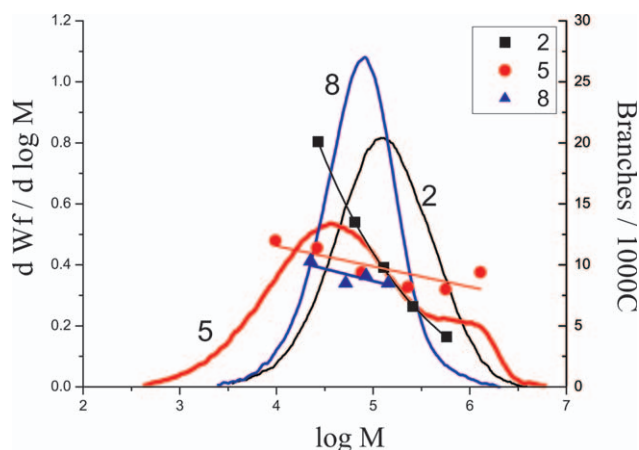
Figure 5 GPC curves and branching distribution in ethylene/1–hexene copolymers with the 10–11 $CH_3/1000C$ branching (numbering of experiments corresponds to Table I). [Color figure can be viewed in the online issue,
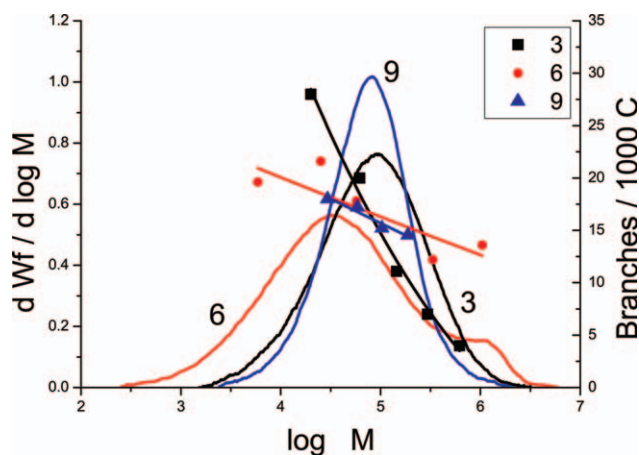
Figure 6 GPC curves and branching distribution in ethylene/1–hexene copolymers with the 16–20 $CH_3/1000C$ branching (numbering of experiments corresponds to Table I). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
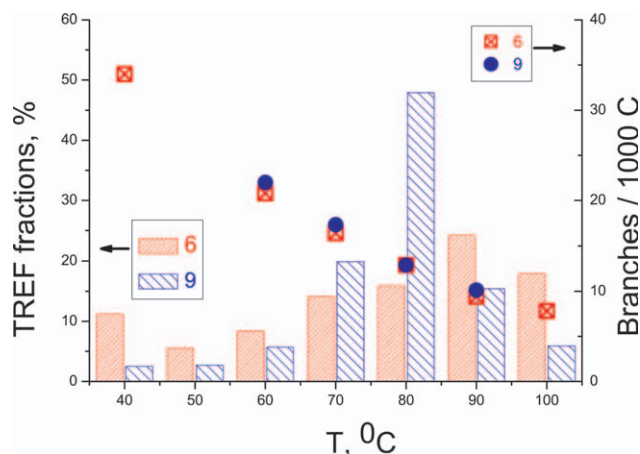
Figure 7 TREF results for ethylene/1–hexene copolymers obtained over VMC (exp. 6, Table I) and zirconocene catalysts (exp. 9, Table I). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

butyl branches (28.2 Bu/1000C) was found in the low molecular weight fraction F1, the contribution of which to the total polymer is high (23.1 wt %). This fraction has quite a broad MWD, which may also be related with the high content of comonomer that provides a better solubility of this fraction even with a large amount of 2-(2-butoxyethoxy)-ethanol. High molecular weight fractions F4 and F5 have a narrow MWD and are low branched (7 and 4 Bu/1000C, respectively).

Table III and Figure 3 present the data on the fractionation of the copolymer produced over VMC (exp. 6, Table I). Noteworthy is a rather broad MWD of the last two fractions of this copolymer, which may be attributed to the very high molecular weight of these fractions. In distinction to TMC, copolymer produced over VMC is more homogeneous; the difference in the composition of individual fractions is only 1.2-fold (Table III) and the content of butyl branches in fractions F5 and F6 remains at a level of 12–14 C_4H_9/1000C. Thus, ethylene/1–hexene copolymer produced over VMC is characterized by a broad bimodal MWD and a higher compositional homogeneity. It seems interesting that the ^{13}C NMR spectrum of the low molecular weight fraction of copolymer F1 produced over VMC includes signals not only from butyl branches and terminal methyl groups, but also the low intensity signals from methyl branches. Earlier, we have found such signals for homopolymer produced over VMC and suggested a scheme of their generation due to internal isomerization of the polymer chain.[19] Such signals are absent in the case of copolymers produced over TMC and zirconocene catalyst.

Table IV and Figure 4 show the data on fractionation of ethylene/1–hexene copolymer produced over the supported zirconocene catalyst (exp. 9, Table I).

Fractions identified in this copolymer have a rather narrow MWD and a close content of butyl branches. A homogeneous distribution of comonomer in this copolymer agrees well with the literature data on comonomer distribution for metallocene systems.[3,6,9]

Figures 5 and 6 depict MWD curves and a profile of branching distribution for copolymers of different composition produced over TMC, VMC, and zirconocene catalyst: data for copolymers with the 10–11 CH_3/1000C branching are shown in Figure 5, and data for copolymers with a higher branching attaining 16–20 CH_3/1000C are shown in Figure 6. As seen from Figures 5 and 6, copolymers produced over VMC and zirconocene catalyst have close profiles of branching distribution, but strongly differ in their MWD (a broad bimodal distribution for VMC and a narrow one in the case of zirconocene catalyst). These systems allow to obtain copolymers with a more uniform distribution of comonomer and, what is especially important, with a higher comonomer content in the region of high molecular weights. As comonomer content increases, heterogeneity of butyl branching distribution becomes somewhat higher (Fig. 6), but the distribution in copolymers produced over VMC and zirconocene catalyst still remains more homogeneous as compared to that in TMC copolymers.

Two copolymers obtained over VMC and zirconocene catalysts (samples 6 and 9 from Table I) were separated by TREF for a more detailed analysis of the molecular structure (Fig. 7). The branching content in fractions eluted at the same temperature for both copolymers are practically the same. It means that separation according to composition was reproducible and each elution temperature corresponds to the definite branching content. It should be noted that the eluted fractions of copolymer produced over VMC have a broad MWD. From Figure 7 one can see a great difference in the relative amounts of fractions for these two copolymers. For the copolymer produced with zirconocene catalyst, it's major par was eluted at 80°C (about 50 wt %). Fractions obtained at 70°C and 90°C are also representative (about 20 and 15 wt % correspondingly). Relative amounts of other fractions are much smaller (lower then 5 wt %). As a result, most part of the polymer was eluted at 70–90°C (about 85 wt %). On the contrary, for the copolymer synthesized over VMC, representative fractions were obtained in whole temperature interval and the highest part of copolymer (about 24 wt %) was eluted at 90°C. As a result, the relative amount of fractions separated at 40–60°C was about 25 wt % in the copolymer, synthesized over VMC and only 11 wt %, in copolymer, synthesized over zirconocene catalyst. It means that the copolymer, produced over supported zirconocene catalyst, is much more homogeneous than one,

obtained over VMC. Data of Figure 7 in conjunction with Figure 6 show that when we determined SCB content vs. molecular weight for copolymer, obtained over VMC, we have measured average values from broad interval of data points (between 8 and 34 branches/1000C). In the case of copolymer, synthesized over zirconocene catalyst, average points most probably arose from narrower interval (between 10 and 17 branches/1000 C).

CONCLUSIONS

It was demonstrated that in the case of VMC, copolymers with various composition have broad MWD and a more uniform profile of SCB content vs. molecular weight as compared to copolymers produced over TMC. These data indicate a higher homogeneity of the VMC active sites with respect to their copolymerization ability in comparison with TMC. The profiles of SCB content vs. molecular weight for copolymers produced over VMC and supported zirconocene catalysts are similar. At the same time TREF data indicate a more homogeneous comonomer distribution in copolymer produced over zirconocene catalyst in comparison with VMC.

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