Heterogeneity of Active Sites of Ziegler-Natta Catalysts: The Effect of Catalyst Composition on the MWD of Polyethylene

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ABSTRACT: Experimental data on the molecular weight distribution (MWD) of polyethylene (PE) produced over a broad number of Ziegler-Natta catalysts differing in composition and preparation procedure are presented. These catalysts include nonsupported $TiCl_3$ catalyst, four types of supported titanium-magnesium catalysts (TMC) differing in the content of titanium and the presence of various modifiers in the composition of the support, and a supported catalyst containing VCl_4 as an active component instead of $TiCl_4$. The studied catalysts produce PE with different molecular weights within a broad range of polydispersity (M_w/M_n = 2.8–16) under the same polymerization conditions. The heterogeneity of active sites of these catalysts was studied by deconvolution of experimental MWD curves into Flory components assuming a correlation between the number of Flory components and the number of active site types. Five Flory components were found for PE produced over nonsupported $TiCl_3$ catalysts (M_w/M_n = 6.8), and three–four Flory components were found for PE produced over TMC of different composition. A minimal number of Flory components (three) was found for PE samples (M_w/M_n values from 2.8 to 3.3) produced over TMC with a very low titanium content (0.07 wt %) and TMC modified with dibutylphtalate. It was shown that five Flory components are sufficient to fit the experimental MWD curve for bimodal PE (M_w/M_n = 16) produced over VMC. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2432–2439, 2010

Key words: Ziegler-Natta catalysts; polyethylene (PE); molecular weight\mass distribution; gel permeation chromatography (GPC); computer modeling

INTRODUCTION

Supported Ziegler-Natta type catalysts, namely, titanium-magnesium catalysts (TMC) are widely used in industry for the production of polyethylene (PE) with various molecular weight (MW) and molecular weight distribution (MWD). The active component of these catalysts is titanium tetrachloride supported on magnesium chloride. A lot of TMC modifications are known that vary in the way of preparation procedure of the support and differ in terms of the composition of titanium compound and the presence of various modifying additives, for example, electron-donor compounds are used for preparation of the support or the catalyst. However, the information on the effect of catalyst composition on MW and MWD of PE is scarce; some data on the MWD of polyethylene produced over Ti-based catalysts are presented in the review[1] and in Ref. (2–17). Polydispersity values (PD = M_w/M_n) for PE produced over TMC usually lie within the range of 4–8.[1–5] Vanadium-magnesium catalysts (VMCs) containing vanadium compound as the active component supported on magnesium dichloride produce PE with a broad MWD; M_w/M_n values usually lie within the range of 10–25.[6–10] The control of MW and MWD of polyethylene is one of the most important problems in ethylene polymerization over supported Ziegler-Natta catalysts. The heterogeneity of the active sites of these multisite catalysts is supposed to be the main reason for MWD broadening ($M_w/M_n > 2$). A number of works is devoted to the analysis of heterogeneity of active sites in Ziegler-Natta catalysts.[3–5,11–14] However, the nature of this heterogeneity remains unclear.

For detailed MWD analysis, we used deconvolution of experimental MWD curves of polymers into several Flory components. This method of analysis of the heterogeneity of active sites in Ti-based Ziegler-Natta catalysts is widely used in the literature.[3,4,11,13–15] A measure of discrepancy between the resulting MWD (obtained by summing all Flory components) and the initial experimental MWD curve is one of the main issues being discussed. Soares and Hamielec[11] proposed to increase the

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number of Flory components until the sum of squares of the residuals (the difference between experimental MWD and theoretical fitting) stops to improve significantly by adding another site type. We believe that they use a very thorough fitting (much more precise than the MWD measurement experimental error). Using this approach, they have found six Flory components for polymer with polydispersity of 4.3. In further work, Soares[14] proposed using additional variance σ^2 in Flory function. This procedure allows decreasing the number of Flory functions required, and as a result, the number of groups of active sites in the catalyst. It was shown that choosing a suitable σ^2 value permits to use even one site type for describing the MWD of PE produced over Ziegler-Natta catalyst, and thus using variance in the calculation should be very careful. Soares proposed using multivariable parameter estimation techniques for adequate describing of the number of active sites in Ziegler-Natta catalysts (not only MWD deconvolution, but also chemical composition distribution or stereoregularity in the case of polypropylene). Another attempt to decrease the number of active sites (Flory components) in supported Ti-based Ziegler-Natta catalyst from five (rigorous MWD curve deconvolution for homo- and copolymers produced) to two–three chemically distinct types was made in.[13]

Kissin et al.[4,16] found that four–five Flory components are often required to adequately describe the MWD of homo- and copolymers produced over Ti-based Ziegler-Natta catalyst (depending on polymerization conditions). They used $TiCl_4/Mg(OEt)_2/SiO_2$ catalyst containing 3 wt % Ti and revealed that hydrogen reduced the catalyst activity and decreased MW of PE due to shifting of all Flory components to lower MW with practically the same contribution of each Flory component. On the contrary, the introduction of hexene-1 was shown to increase the contribution of lower MW sites while all peak positions of Flory components stay the same.

The active site distribution of TMC doped with various inorganic compounds in the support was studied via nonlinear fitting of polymer GPC curves by multiple Flory components in Ref. 17,18. Chen et al.[17] investigated ethylene polymerization over four TMC doped with different $AlCl_3$ content. They showed that doping of catalyst with $AlCl_3$ allows increasing M_w (from 195×10^3 to 238×10^3) and M_w/M_n value greatly (from 10.8 to 23.8). It should be noted that these very high M_w/M_n values are rather unusual for TMC. The deconvolution results revealed five types of active sites to exist in undoped $MgCl_2$-supported catalyst ($M_w/M_n = 10.8$) and six types of active sites to exist in $AlCl_3$-doped $MgCl_2$-supported catalyst ($M_w/M_n = 17.6$ for 14.5% $AlCl_3$ and $M_w/M_n = 23.8$ for 28.7% $AlCl_3$).

In this work, we used a wide set of highly active supported Ziegler type catalysts of various composition that allow one to regulate MWD of PE over a wide range ($M_w/M_n = 2.8$–16). Among them, there are four samples of TMC differing in the content of titanium and the presence of various modifications [internal donor (dibutylphtalate) and ethoxy groups in the catalysts], and one sample of VMC. The nonsupported $TiCl_3$ catalyst is also used for comparison with supported TMC.

As few as possible Flory functions were used for deconvolution of experimental MWD curves with an accuracy of ca. 1–1.5% in standard deviation value. We consider that such values correspond to experimental accuracy of defining MWD curves. MathCAD program was used to perform this algorithm.

Using this method, the effect of catalyst composition on MWD of PE and heterogeneity of active sites for Ziegler-Natta catalysts with various compositions producing PE with M_w/M_n values within the range 2.8–16 were examined.

EXPERIMENTAL

Catalysts

$TiCl_3$ is the commercial sample of Solvay type catalyst.

TMC with different titanium content, TMC-0.07 (0.07 wt % of Ti) and TMC-3 (3 wt % of Ti), were synthesized via a procedure described earlier[2,19] by supporting titanium tetrachloride on highly dispersed magnesium dichloride with the average particle size of 10 μm and narrow particle size distribution.

TMC*D catalyst modified with dibutylphtalate (DBPh) was obtained as follows. A solution of the complex with composition $2\ Mg(OEt)_2 \cdot Ti(OBu)_4$ in PhCl with added DBPh (DBPh/Ti = 1) was treated with $TiCl_4$ at $TiCl_4/Mg$ molar ratio = 2. Then, the solid product was additionally treated with $TiCl_4$ at 128°C and Ti/Mg molar ratio = 1. Catalyst TMC*D contains 2.2 wt % of Ti and 15.6 wt % of DBPh.

TMC-*OR catalyst (2.6 wt% of Ti) was synthesized via a procedure described elsewhere[20] by supporting titanium tetrachloride on the support prepared by interaction of a solution of organomagnesium compound $Mg_3Ph_4Cl_2$ in dibutyl ether and PhCl with the mixture of $PhSiCl_3$ and $Si(OEt)_4$ at $PhSiCl_3/Si(OEt)_4$ molar ratio = 3.

VMC was obtained via a procedure described elsewhere[21] by supporting vanadium tetrachloride on magnesium dichloride support. The support was prepared by interaction of magnesium organic compound $Mg_3Ph_4Cl_2$ dissolved in the mixture of PhCl and dibutyl ether with CCl_4. Thus, the obtained support was additionally treated with diethylaluminum

TABLE I
Data[a] on the Effect of Catalyst Composition on the Activity and MWD of PE

	Catalyst	Content of Ti, (wt %)	Yield, kg PE/g_{cat}	Activity, kg PE/g Ti × h × bar C_2H_4	PE No.	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$	M_w/M_n	M_z/M_w
I	$TiCl_3$	27.5	2.4	2.0	1	40	270	1200	6.8	4.4
II	$TiCl_4/MgCl_2$ (TMC-3)	3.0	4.0	33	2	50	250	810	5.0	3.2
III	$TiCl_4/MgCl_2$ (TMC-0.07)	0.07	1.2	460	3	55	180	480	3.3	2.7
IV	$TiCl_4/MgCl_2 \cdot$ DBPh (TMC *D)	2.2	2.0	23	4	75	210	420	2.8	2.0
V	$TiCl_4/MgCl_2$ (TMC-*OR)	2.6	5.6	54	5	24	125	390	5.2	3.1
VI	$VCl_4/MgCl_2$ (VMC)	3.2[b]	4.3	17[c]	6	22	340	1470	16.0	4.4

[a] Polymerization conditions: 80°C, TIBA as a cocatalyst, ethylene pressure 4.0 bar, and the ratio of $H_2/C_2H_4 = 0.25$ in exp. 1–5; ethylene pressure 8.0 bar, and the ratio of $H_2/C_2H_4 = 0.125$ in exp. 6.
[b] Content of V.
[c] kg PE/g V × h × bar C_2H_4.

chloride and CCl_4. The catalyst contained 3.2 wt % of vanadium and 1.4 wt % of aluminum.

Ethylene slurry polymerization

Ethylene slurry polymerization was performed in a 0.85 L steel reactor, in *n*-heptane under constant ethylene pressure, in the presence of hydrogen as chain transfer agent, and at polymerization temperature of 80°C for 1 hour; triisobutylaluminum (TIBA) was used as a co-catalyst; its concentration being 4.8–5.6 mmol TIBA/L, and the catalyst concentration being 0.02–0.04 g/L. The pressure of ethylene was 4 bar and pressure of hydrogen was 1 bar for polymerization over TMC. The pressure of ethylene was 8 bar and the pressure of hydrogen was 1 bar for polymerization over VMC.

MWD measurements

MWD measurements were performed using a PL 220C instrument with RI and DV detectors. Run conditions were as follows: temperature was 160°C, and 1,2,4-trichlorobenzene was used as a solvent at a flow rate of 1 cm^3/min. Four mixed bed TSK-gel columns (GMHXL-HT, Tosoh Corp.) were used. Universal Calibration was made using narrow Polystyrene standards and PE standards.

Deconvolution of MWD curves

Deconvolution of MWD curves was based on the approach described elsewhere.[3,13,14] It was assumed that in multisite catalysts each type of active sites produces a polymer with Flory distribution. For each Flory distribution, $w(n, a)$, the most probable Flory distribution function for polymer consisting of n monomer units produced at a type j site is given by

$$w(n, a_j) = 2.3026\, a_j^2\, n^2 \exp(-a_j\, n), \tag{1}$$

where a_j is the ratio of chain transfer to chain propagation rates at type j site.

This function has characteristic asymmetric GPC profiles, and their MWD corresponds to $M_w/M_n = 2$.

Therefore, the overall MWD of the polymer (composed of the individual Flory components) is

$$W(n) = \sum_{j=1} m_j\, w(n,\, a_j), \tag{2}$$

where $W(n)$ is the weight distribution of the polymer consisting of n monomer units, and m_j is the weight fraction of polymer produced by type j site.

The active site parameters, a_j and m_j, were estimated using nonlinear least-squares regression to minimize function $F(m_j, a_j)$ with an accuracy of ca. 1–1.5% in standard deviation value. MathCAD was used for this algorithm.

$$F(m_j, a_j) = [q^{\exp}(n) - \sum_{j=1} m_j w(n, a)]^2, \tag{3}$$

where $q^{\exp}(n)$ is the experimental GPC data.

Standard deviation was calculated as

$$\sigma = 100 \cdot \sqrt{\frac{1}{n}\sum_{i=1}^{n}(W - W_{\exp})^2}, \tag{4}$$

where n is the total number of points of MWD distribution, W is the sum of all Flory components in point i, and $W_{\exp}$ is the experimental value of MWD distribution in point i.

RESULTS AND DISCUSSION

Effect of catalyst composition on MWD of PE

The data on the activity of catalysts in ethylene polymerization and the data on the MWD of PE

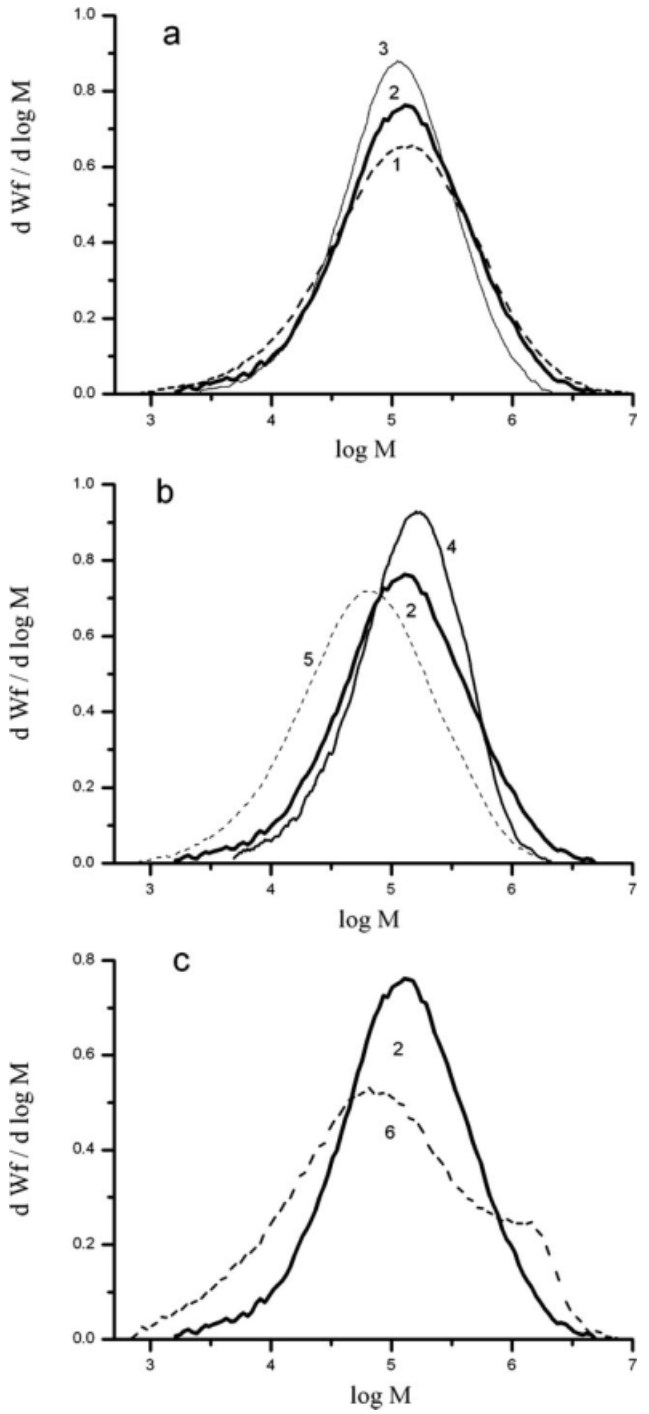

Figure 1 (a–c) The GPC curves of PE produced over $TiCl_3$ (curve 1), TMC-3 (curve 2), TMC-0.07 (curve 3), TMC *D (curve 4), TMC-*OR (curve 5), and VMC (curve 6) (see Table I, PE samples 1, 2, 3, 4, 5, 6).

produced with different types of catalysts are presented in Table I and Figure 1(a,b,c). Some kinetic data on ethylene polymerization over catalysts II, III and VI were given more minutely in our previous articles.[2,7,8] Here, we focus the main attention on the analysis of MWD curves for PE produced over the catalysts of various compositions. In this study, we used the nonsupported $TiCl_3$ catalyst and four samples of TMC differing in titanium content (TMC-0.07 and TMC-3), presence of internal donor (DBPh) (TMC*D), and ethoxy groups in the catalysts (TMC-*OR).

The nonsupported $TiCl_3$ catalyst produced polymer with a broader MWD as compared to PE obtained over supported TMC catalysts [see the data for PE 1, PE 2 and PE 3 samples in Table I and Fig. 1(a)]. The broadening of MWD of PE produced over $TiCl_3$ catalyst in comparison with TMC-3 was caused by the formation of mainly low-molecular part of PE [curves 1 and 2, Fig. 1(a)].

The decrease in titanium content in supported titanium magnesium catalysts resulted in the decrease of M_w and M_w/M_n values of PE [M_w decreased from 250×10^3 to 180×10^3 and M_w/M_n decreased from 5.0 to 3.3 (see the data for PE 2 and PE 3 in Table I)]. It can be seen that narrowing of MWD arises from the disappearance of the high-molecular part in PE 3 sample as compared to PE 2 [see curves 2 and 3 in Fig. 1(a)]. Thus, the data presented in Table I and Figure 1(a) for samples PE 1, PE 2, and PE 3 show that the deposition of titanium compound on $MgCl_2$ support resulted in narrowing the MWD of polyethylene produced. In the case of supported catalyst with a higher Ti content, the disappearance of the low MW shoulder is observed, whereas in the case of catalyst with a low Ti content, the high-molecular shoulder disappeared. Overall, this resulted in considerable narrowing of MWD (the PD value decreased from 6.8 to 3.3).

We found that the addition of alkylaromatic ether (DBPh) into composition of TMC (TMC-*D catalyst) led to the formation of polyethylene with the narrowest MWD [sample PE 4, Table I, Fig. 1(b)]. The addition of DBPh into TMC resulted in decreasing the PD values from 5.0 (PE 2, catalyst TMC-3) to 2.8 (PE 4, catalyst TMC-*D). As seen from Figure 1(b), PD decreased due to the elimination of both high- and low-molecular parts of PE.

The addition of ethoxy groups into the composition of the catalyst (TMC-*OR catalyst) led to the formation of PE with a lower M_w (sample PE 5, Fig. 1b) in comparison with TMC-3 [sample PE 2, Fig. 1(b)]. The values of M_n, M_w and M_z for PE produced over TMC-*OR are twice lower in comparison with that produced over TMC-3. Thus, the addition of ethoxy groups into TMC resulted in decreasing the MW and did not change the value of PD ($M_w/M_n = 5.0$–5.2).

The great difference between PE produced over Ti-based catalysts and VMC is observed [Table I, Fig. 1(c)]. VMC produced PE with a broad and bimodal MWD. The M_w/M_n value for PE synthesized with VMC amounts to 16, in contrast to PD values of 2.8–5.2 for PE produced over TMC. The MWD curve for PE produced over VMC

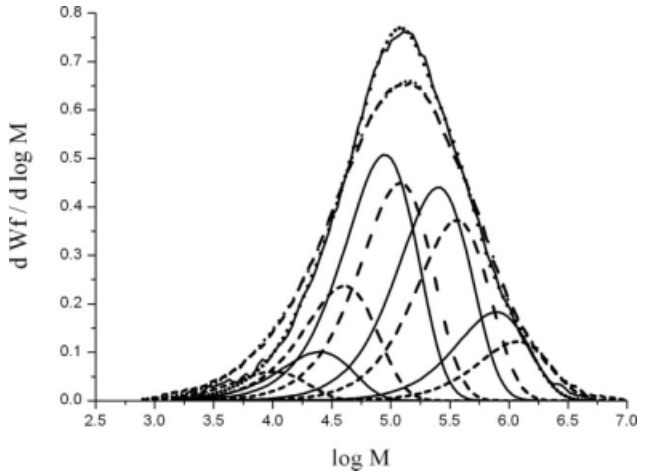

Figure 2 The GPC curves of samples PE 1 (dash curve) and PE 2 (solid curve) and their resolution into Flory components; Dots – calculated MWD curve (the sum of all Flory components).

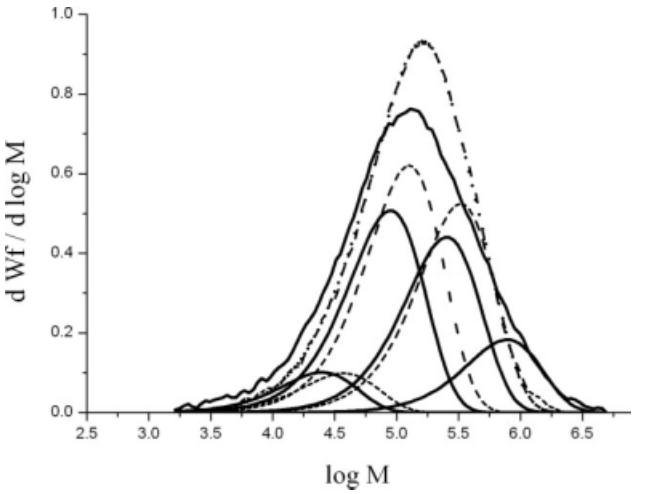

Figure 4 The GPC curves of samples PE 2 (Solid Curve) and PE 4 (Dash Curve) and their resolution into Flory components; Dots – calculated MWD curve (the sum of all Flory components).

demonstrates an explicit shoulder within the high MW region [Fig. 1(c)]. Note, VMC catalysts have a higher hydrogen response (a higher ratio of chain transfer reaction rate constant with hydrogen to propagation reaction rate).[7,8] Therefore, it was necessary to use a lower H_2/C_2H_4 ratio for ethylene polymerization over VMC (Table I, PE 6) in comparison with TMC to get polymers with the close average MW.

Analysis of experimental data via the deconvolution of MWD curves

Experimental data on the effect of catalyst composition on the MWD of PE were used for the analysis of heterogeneity of the active sites via the deconvolution of MWD curves. The results of resolution of GPC curves 1–6 [Fig. 1(a–c)] are presented in Figures 2–6 and Table II. Good fitting of calculated and experimental MWD curves for polymers produced over TMC and VMC is observed (Figs. 2–6). Three types of catalysts and corresponding polymers are analyzed: (i) nonsupported $TiCl_3$ catalysts (PE sample 1); (ii) supported TMC catalysts with different composition (PE samples 2, 3, 4 and 5); (iii) supported VMC (PE sample 6). We found that 3–4 Flory components are sufficient to describe the MWD curves for PE 2–5 produced over supported TMC of various compositions. Sample PE 1 produced over nonsupported $TiCl_3$ catalyst has a broader MWD, and five Flory components are needed to describe this MWD curve (Fig. 2).

The data on the M_w values and weight of individual Flory components are presented in Table II and

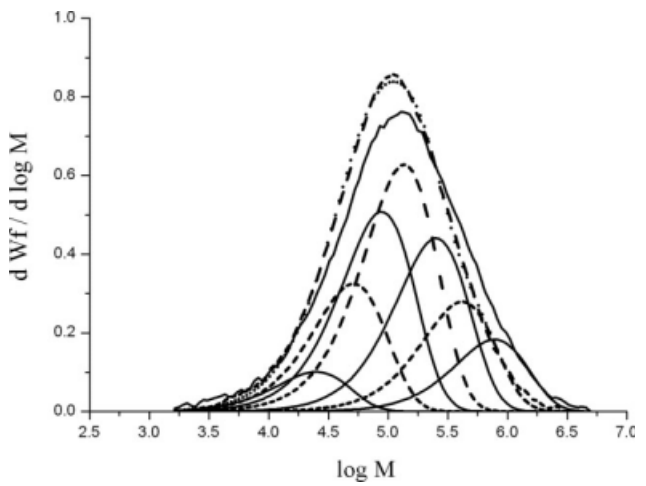

Figure 3 The GPC curves of samples PE 2 (solid curve) and PE 3 (dash curve) and their resolution into Flory components; Dots – calculated MWD curve (the sum of all Flory components).

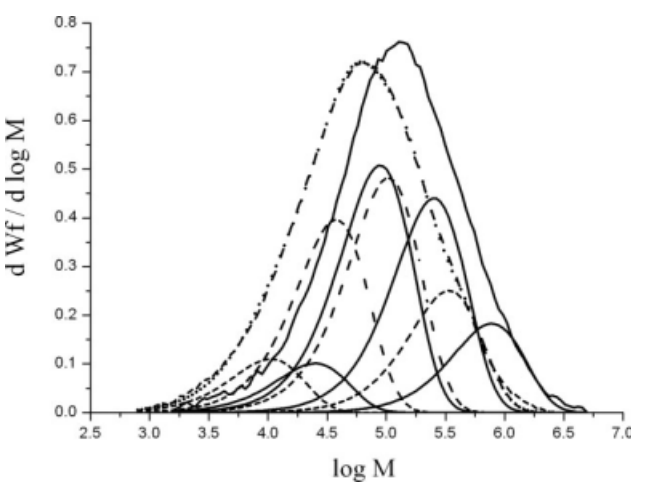

Figure 5 The GPC curves of samples PE 2 (solid curve) and PE 5 (dash curve) and their resolution into Flory components; Dots – calculated MWD curve (the sum of all Flory components).

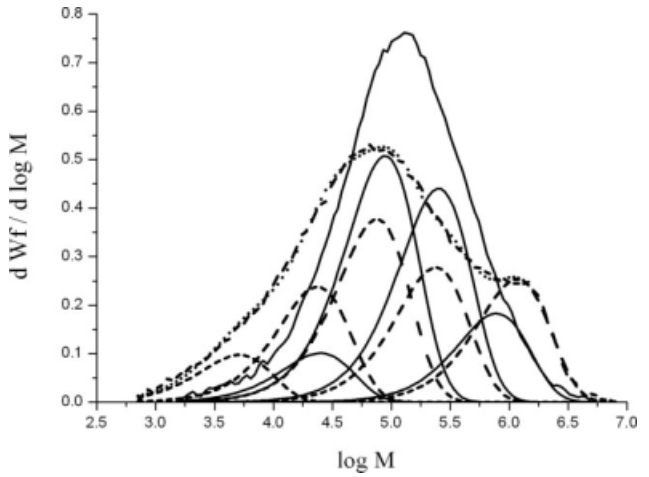

Figure 6 The GPC curves of samples PE 2 (solid Curve) and PE 6 (dash Curve) and their resolution into Flory components; Dots – calculated MWD curve (the sum of all Flory components).

Figures 2–6. The comparison of calculated and experimental MWD curves for polymers produced over TMC and VMC is shown on Figures 2–6. The analysis of these data for PE 1 and PE 2 samples (catalysts $TiCl_3$ and TMC-3, respectively) indicated a slight shift in the positions of components III and IV and sum weights of these fractions (66 – 76.2%). In the case of sample PE 2, the contribution of high-molecular fraction V increased, the contribution of low-molecular component II decreased, and the lowest molecular component I was absent. The overall effect of these changes resulted in a decrease of M_w/M_n value for PE obtained over supported catalyst TMC 3. Thus, nonsupported $TiCl_3$ catalyst was found to have the maximum amount of Flory components among Ti-based catalysts. In the case of TMC-3, the narrowing of MWD was observed mainly from elimination of low-molecular Flory component I and decreases of the portion of component II.

It was found that three Flory components are sufficient to describe the MWD curve for PE 3 sample produced over catalyst with the lowest titanium content (TMC-0.07). It can be seen that the contribution of high-molecular component IV decreased, and the highest molecular component V disappeared from PE 3 sample that resulted in a decrease of M_w value of the entire polymer. Meanwhile, components II, III and IV shifted to high MW region, and the contribution of components II and III into the overall MWD increased (Table II, Fig. 3). It is evident that narrowing of MWD for TMC-0.07 was caused by a decrease in the contribution of high-molecular part of PE as compared to TMC 3.

The addition of DBPh to TMC*D results in the formation of PE 4 sample with the most narrow MWD and a lower M_w value in comparison with PE 2. The

TABLE II
The Results of Deconvolution of MWD curves into Flory components for PE Samples (PE 1 – PE 6 from Table I)

Catalyst	$TiCl_3$		TMC-3		TMC-0.07		TMC *D		TMC-*OR		VMC	
PE[a]	1		2		3		4		5		6	
Flory component	Fraction weight, (%)	$M_w \times 10^{-3}$	Fraction weight, (%)	$M_w \times 10^{-3}$	Fraction weight, (%)	$M_w \times 10^{-3}$	Fraction weight, (%)	$M_w \times 10^{-3}$	Fraction weight, (%)	$M_w \times 10^{-3}$	Fraction weight, (%)	$M_w \times 10^{-3}$
I	4.8	10	–	–	–	–	–	–	–	–	5.2	5.4
II	19.0	40	8.1	25	26.1	52	7.9	38	8.8	11	14.1	24
III	36.1	120	40.8	90	50.4	136	49.8	126	31.8	38	27.5	76
IV	29.9	360	35.4	250	22.4	420	42.1	330	38.7	104	29.3	240
V	9.8	1190	14.7	780	–	–	–	–	20.1	340	23.5	1170
Total polymer M_w[b] $\times 10^{-3}$		280		245		180		205		125		320
M_w/M_n[b]		7.0		4.4		3.2		2.7		4.7		15.5

[a] PE numbers correspond to those in Table I.
[b] Calculated from theoretical (the sum of Flory components) MWD curve.

results of the resolution of GPC curves for PE 4 sample in comparison with PE 2 are presented in Figure 4 and Table II. These data show that an adequate resolution of the MWD curve for PE 4 requires three Flory components. It is seen from the comparative data for PE 2 and PE 4 samples that the addition of DBPh to the catalyst slightly changes the position of Flory components II, III, and IV and led to the disappearance of high-molecular component V. Probably, DBPh added into the catalyst eliminates the catalyst active sites in which the polymer with high MW is produced.

The addition of ethoxy groups into the composition of TMC decreased the MW of PE 5 in comparison with PE 2 produced with TMC-3. It was found that four Flory components are necessary for adequate resolution of the MWD curve for PE 5. The data (Table II, Fig. 5) show that all Flory components shifted to the low MW region. It is seen from the comparative data for PE 2 and PE 5 samples that the addition of ethoxy groups into the composition of TMC decreases the M_w value for all Flory components. It provides a twofold decrease in the MW with the retention of M_w/M_n value. Thus, OR groups of the support equally affected all groups of active sites in catalysts similar to TMC-3.

The MWD of PE 6 sample produced over VMC is much broader than the MWD of PE 2 sample produced over TMC-3 (M_w/M_n values are 16.0 and 5.0, respectively). The results of resolution of GPC curve for PE 6 into Flory components in comparison with PE 2 sample are presented in Figure 6 and Table II. Five Flory components are sufficient to describe the MWD curve for PE 6 produced over VMC. The following main differences in comparison with PE 2 sample are observed:

(i) A new low molecular component I was formed;
(ii) The position of high MW component V shifted to the high molecular region and the portion of this component increased;
(iii) A more homogeneous contribution of components II-V is observed for PE 6 sample (14.1–29.3%) in comparison with PE 2 sample (10.7–39.9%), with main components III and IV constituting 73.7%.

Finally, this results in a much broader MWD of PE 6 sample in comparison with PE 2 sample.

Unfortunately, only a few experimental data on the structure of the surface titanium species formed in TMC are available for the discussion of the origin of heterogeneity of the active sites that produce PE with broad MWD.

In this connection, it should be noted that the effect of titanium oxidation state on the MWD of PE produced with different samples of TMC, which was prepared using titanium compounds in different oxidation states (Ti (IV), Ti (III) and Ti (II)), was analyzed recently.[22,23] We did not find a significant effect of this parameter on MWD of PE produced. Therefore, it can be assumed that the distinctions in reactivity of the active sites of TMC, which result in the formation of polymers with different MWs, are determined mainly by the structure of surface titanium compounds (coordination number, presence of additional ligands and components in first or second coordination sphere of titanium ion). TMC-0.07 catalyst with low Ti content is a convenient object for identification of possible structures of active sites. According to the earlier obtained data,[2,23] this catalyst possesses a significantly higher activity in comparison with catalyst TMC-3 and makes it possible to produce PE with a narrower MWD. The activity of TMC abruptly decreases with increasing Ti content by more than 0.1 wt %. The enhanced activity of TMC-0.07 is associated with a higher amount of active sites that attains 55% of the total Ti content.[2] It can be assumed that in this catalyst four coordinated magnesium ions located on the (110) surface have higher acidity in comparison with five coordinated magnesium ions on the (104) surface and, probably, $TiCl_4$ interacts first with the sites on the (110) surface. However, according to the estimates presented in Ref. 24,25 the portion of the surface sites of activated magnesium chloride that are located on the (110) surface and interact with titanium chloride is sufficiently small and comprises no more than 10% of the portion of those located on the (104) surface. A subsequent increasing of Ti content results in the formation of surface titanium compounds on the (104) surface. It leads to a sharp decrease in the activity per unit weight of titanium; however, the total yield of polymer per gram of the catalyst increases. This proves that additional active sites are formed on the (104) surface; however, the fraction of the active sites with respect to the total Ti content considerably decreases and does not exceed 10% of the Ti content.

PE produced with the TMC-0.07 catalyst has the M_w/M_n value 3.3, and its MWD curve can be resolved into three Flory components. Thus, even if the active sites are formed only on the (110) surface, the formation of several structures, for example, due to adsorption of AlR_2Cl produced upon the activation of TMC by triethyl aluminum is possible.[26] Examples of such structures are presented in Ref. 26. A further increase in Ti content leads to the appearance of surface titanium compounds on the surface (104) with the formation of new structures among which three structures are close in their properties to those on the surface (110) (Flory components I, II,

III for samples PE 2 and PE 3), and a new structure on which high-molecular polymer (component V for PE 2) is formed.

CONCLUSION

The heterogeneity of active sites of Ziegler-Natta catalysts with different composition (nonsupported $TiCl_3$ catalyst, four types of supported TMC differing in the content of titanium and the presence of various modifiers in the composition of support, and supported VMC) has been studied via deconvolution of experimental MWD curves of PE samples prepared over these catalysts.

TMC catalysts of various compositions allow producing PE with PD values within the range 2.8–5.2. TMC with high Ti content (TMC-3) and TMC modified by ethoxy groups (TMC-*OR) produce PE with more broad MWD (M_w/M_n = 5.0–5.2). The results of resolutions of experimental GPC curves into Flory components indicate that four Flory components are sufficient to describe MWD curves of PE produced over TMC-3. The addition of ethoxy groups into the composition of TMC-*OR proceeds to two-fold reducing of MW of PE in comparison to PE produced with TMC-3catalyst. The M_w/M_n value remains invariant and the amount of Flory components does not change. It was shown that the decrease in MW of all Flory components leads to two-fold decrease in MW of PE produced over TMC-*OR catalyst.

Catalyst with low Ti content (TMC-0.07) produce PE with lower M_w value and with more narrow MWD (M_w/M_n = 3.3). Three Flory components are necessary to fit MWD curve of PE produced over TMC-0.07 (as compared to four Flory functions for PE produced over TMC-3). The narrowing of MWD and decreasing of M_w value of PE produced over TMC-0.07 is caused by the disappearance of high molecular Flory component. The addition of DBPh to TMC (TMC-*D) results in formation of PE with lower M_w value and more narrow MWD as compared to PE produced over TMC-3, due to the elimination of high-molecular part of PE.

Nonsupported $TiCl_3$ catalyst produces PE with rather broad MWD (M_w/M_n = 6.8). Five Flory components are necessary to fit MWD curve for this polymer. MWD broadening is caused by the formation of additional Flory component in the low-molecular part of PE and increases of the portion of low MW components I and II.

The great difference between PE produced over Ti-based catalysts and VMC was revealed. VMC produces PE with broad and bimodal MWD. It was found regardless of very broad MWD (M_w/M_n = 16). Five Flory components are sufficient to fit MWD curve of PE produced with VMC. The formation of the new low MW component and increase of portion of high MW Flory component were shown to be the reason of MWD broadening for VMC.

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