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Ethylene Polymerization over Supported Titanium-Magnesium Catalysts: Heterogeneity of Active Centers and Effect of Catalyst Composition on the Molecular Mass Distribution of Polymer

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Summary: New experimental approach was used for analysis of molecular weight distribution (MWD) of polymers produced over titanium-magnesium catalysts (TMC). Polymers were fractionated on to fractions with narrow MWD (polydispersity (PD) values Mw/Mn $\leq$ 2). Then some of these fractions were combined to get the minimal quantity of fractions with PD values close to 2 (Flory components). It was found that three fractions corresponding to three groups of active centers are sufficient for proper fitting experimental MWD curve for PE obtained over TMC with different Ti content and with different hydrogen concentration in polymerization.

Keywords: fractionation of polymers; molecular weight distribution/molar mass distribution; polyethylene (PE); titanium-magnesium catalysts (TMC); ziegler-natta polymerization

Introduction

One of the most important problems in ethylene polymerization over supported Ziegler-Natta catalysts is the control of molecular weight (MW) and molecular weight distribution (MWD) of polyethylene (PE). The most famous supported Ziegler-Natta type catalysts are titanium-magnesium catalysts (TMC) which produce PE with rather broad MWD. Polydispersity values (PD = Mw/Mn) for PE produced with TMC are usually within the range of $4 \div 8$.[1,2] It is supposed that the main reason for MWD broadening (Mw/Mn > 2) is heterogeneity of the active centers of these catalysts (multisite catalysts). However, the nature of this heterogeneity remains unclear.

There are several concepts of theoretical analysis of MWD curves.[3–6] These approaches lead to the different results on the quantity of the separate groups of active centers (five or three) in the TMC and to our mind they are ambiguous for complete description of the heterogeneity of active centers of Ziegler-Natta type catalysts.

In the present work we used the new experimental approach for analysis of heterogeneity of active centers in the supported TMC (fractionation of PE for narrow fractions with following construction of MWD according to fractionation data). Highly active supported TMC with optimal morphology and controlled Ti content have been used in this study. Recently[2] we have presented some data on the activity of these catalysts and effects of Ti content and hydrogen content at polymerization on the MWD of PE produced. Based on these data we have selected TMC with low and high Ti content for the more detailed analysis of the heterogeneity of active centers of TMC by fractionation of PE samples for narrow fractions with following construction of MWD curves.

Experimental Part

Catalysts were synthesized via procedure described elsewhere[2,7] by supporting of

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titanium tetrachloride on highly dispersed magnesium chloride with average particle size 10 μm and narrow particle size distribution. Two catalysts with Ti content of 0.07 wt. % (TMC-0.07) and 5 wt. % (TMC-5) have been used in this study.

Ethylene slurry polymerization was performed in a 0.8 L steel reactor, in heptane, at constant ethylene pressure 4 bar and polymerization temperature 80 °C for 1 hour; triisobutylaluminium (TIBA) was used as a co-catalyst, its concentration being 2–10 mmol TIBA/L, catalyst concentration was 0.04 g/L.

MWD measurements were performed using a WATERS-150 C instrument in conjunction with Differential Viscometer (Viscotek Model 100). Run conditions were as follows: temperature 140 °C; 1,2,4-trichlorobenzene (TCB) 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. Calibration was made using narrow Polystyrene standards and PE standards.

Fractionation of PE samples for narrow fractions was made on fractionation station of PolymerChar company ''PREP mc2''. Xylene and diethylene glycol monobutyl ether was used as a solvent and non-solvent accordingly. PE was dissolved in xylene at 130^0C. Non-solvent contents in the mixture with solvent were 51%; 43%; 40%; 38% and 0% to get 5 narrow fractions F1; F2; F3; F4; F5.

Results and Discussion

The data on the effect of Ti content on the activity of TMC and MWD of PE are presented in Table 1. The activity of TMC-0.07 is about ten times higher then that of TMC- 5. It was shown[2] that the reason of higher activity of TMC with low Ti content is the higher number of active centers. Similar Kp values for ethylene polymerization over TMC with different Ti content (0.1 and 0.9 wt. % of Ti) were found.[8]

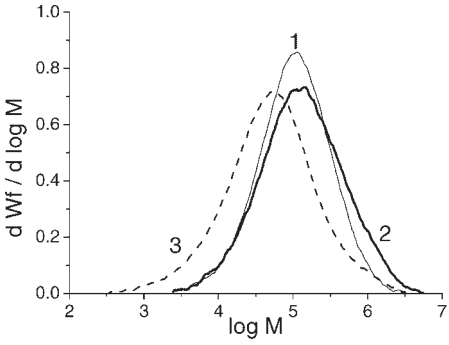

Figure 1.
GPC curves of PE produced over TMC-0.07 (curve 1) and TMC-5 (curve 2 and 3), see Table 1, exps. 1, 2, 3 accordingly.

The increase of titanium content in TMC results in the increase of Mw value of PE (Mw increases from 180×10^3 up to 280×10^3) and increase PD value from 3.1 to 4.8 (exp 1 and 2 in Table 1). Mn values change slightly and remain within the range of $(57 \div 58) \times 10^3$. It is seen that the MWD broadening arises from the high-molecular-weight part of PE (see curves 1 and 2 in Figure 1).

The data on the effect of hydrogen content (H_2/C_2H_4 ratio) on MWD of PE produced over the catalyst with higher titanium content (5 wt.-%.) are also shown in Table 1 and Figure 1 (curves 2 and 3). It is evident that the increase of hydrogen content not only decreases MW of PE

Table 1.
Data on the effect of Ti content on the activity of TMC, MW and MWD of PE.

Catalyst	PE No.	$[H_2]/[C_2H_4]$	Activity, Kg PE/g Ti × h × bar C_2H_4	Mn × 10^{-3}	Mw × 10^{-3}	Mz × 10^{-3}	PD
TMC-0.07	1	0.25	460	57	180	420	3.1
TMC-5	2	0.25	48	58	280	940	4.8
TMC-5	3	1	26	17	130	650	7.7

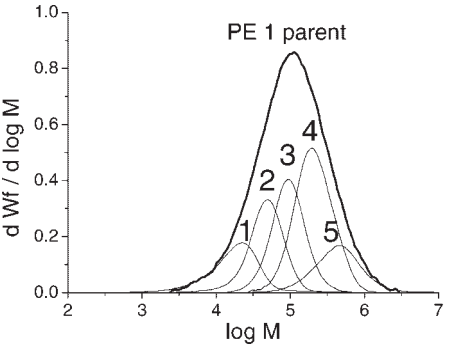

Figure 2.
GPC curves of narrow fractions, obtained after fractionation of PE sample 1 from Table 1.

(the usual result) but increases the PD value from 4.7 to 7.7. It is seen that as H_2/C_2H_4 ratio increases the MWD peak shifts to the low molecular weight region except the high molecular weight tail.

It is generally supposed the different reactivity of active centers in the propagation reaction leads to the broadening of MWD of PE. However the data presented here allow to suggest the heterogeneity of active centers of TMC in the chain transfer reaction with hydrogen can lead to the broadening of MMD.

We used three polymers (samples 1, 2 and 3 in Table 1) for more detailed analysis of MWD curves via fractionation of these samples for separate fractions with narrow MWD. All three PE samples were fractionated using the same fractionation program in order to obtain five fractions with values of PD ≤ 2. Fractionation results for sample 1 from Table 1 are shown in Table 2 and Figure 2. It is necessary to note that MWD curves of each fraction (Figure 2) were normalized proportionally to its relative amount. One can see from data presented that all fractions have narrow MWD. It is necessary to note the Mz/Mw values for fractions F1 and F5 are higher than 1.5 (3.1 and 2 correspondingly). It is caused by presence of small high molecular weight tails in this fractions and results probably from some limitations of fractionation method. The data for sum of all fractions is close to MWD data of parent sample (Table 2).

As a result of fractionation (Table 2) we obtained two fractions F1 and F5 with Mw/Mn values 2.1 and 1.8 correspondingly, close to Flory distribution (Mw/Mn = 2,) and three fractions F2, F3 and F4 with Mw/Mn values lower then 2 (1.3–1.4). We proposed to combine these three fractions (F2, F3 and F4) into one fraction F* (see Table 3).

New combined F* fraction has narrow MWD close to Flory distribution (Mw/Mn = 2). MWD curves for F1, F* and F5 are presented in Figure 3 in comparison with parent sample. It seems like assumption that three groups of active centers produce three PE fractions with MWD close to Flory type and three types of active centers is sufficient for proper fitting experimental MWD curve (minimal quantity of separate fractions with Mw/Mn values close to 2.0).

The similar results were obtained for PE samples 2 and 3 from Table 1 (see Table 3). We proposed again to combine three medium fractions (F2, F3 and F4) for

Table 2.
Experimental fractionation data of the sample 1 from Table 1.

Polymer fraction	Amount of the fraction, %	Mp $\times 10^{-3}$	Mn $\times 10^{-3}$	Mw $\times 10^{-3}$	Mz $\times 10^{-3}$	Mw/Mn	Mz/Mw
Parent PE	100	110	55	180	480	3.3	2.6
F1	13	22	12	25	78	2.1	3.1
F2	19	49	38	53	70	1.4	1.3
F3	23	96	82	110	145	1.3	1.3
F4	32	200	170	240	330	1.4	1.4
F5	13	500	325	590	1200	1.8	2.0
Sum[a)]	100	130	48	180	570	3.8	3.2

[a)] Sum = F1 + F2 + F3 + F4 + F5.

Table 3.
Calculated data for fractionated polymers after conjunction of central fractions.

Parent PE sample	Polymer	Weight of the fraction, %	Mp $\times 10^{-3}$	Mn $\times 10^{-3}$	Mw $\times 10^{-3}$	Mw/Mn
1	Parent[a)]	100	110	55	180	3.3
	F1	13	23	12	26	2.2
	F*	74	115	76	150	2.0
	F5	13	460	305	560	1.8
	Sum[b)]	100	130	48	180	3.8
2	Parent[a)]	100	145	58	280	4.8
	F1	11	18	8.8	19	2.2
	F*	62	100	64	130	2.0
	F5	27	480	390	700	1.8
	Sum[b)]	100	150	44	270	6.1
3	Parent[a)]	100	55	19	130	6.8
	F1	29	17	7.3	15	2.1
	F*	62	61	59	110	1.9
	F5	9	430	380	660	1.7
	Sum[b)]	100	61	20.5	130	6.1

[a)] Experimental MWD data for parent sample;
[b)] Calculated MWD data for sum of F1, F* and F5.

samples 2 and 3 into one fraction F* for each sample (see Table 3 with calculated MWD data) and obtained new calculated fraction F* with narrow MWD (Mw/Mn $\cong$ 2). It is seen again for samples 2 and 3 three groups of active centers produce three PE fractions with MWD close to Flory type and suggestion on three types of active centers is sufficient for proper fitting experimental MWD curves.

Calculated MWD data for separate fractions F1, F* and F5 for samples 1, 2 and 3 from Table 3 are summarized in Figure 4. It is necessary to note that the position (peak maxima) of F5 is close for samples 1, 2 and 3. Position of F* is practically the same for samples 1 and 2 but for sample 3 is shifted toward lower MW. Based on fractionation results (Figure 4 and Table 3) it is possible to discuss the effects of Ti content in TMC and H_2/C_2H_4 ratio at polymerization on the MWD of PE produced over TMC.

It is seen that broadening of MWD of PE at increasing of Ti content in the catalyst (samples 1 and 2) caused mainly due to twice higher amount of F5 fraction of PE with highest MW. So we believe the both catalysts (TMC-0.07 and TMC-5) contain the same group of active centers which

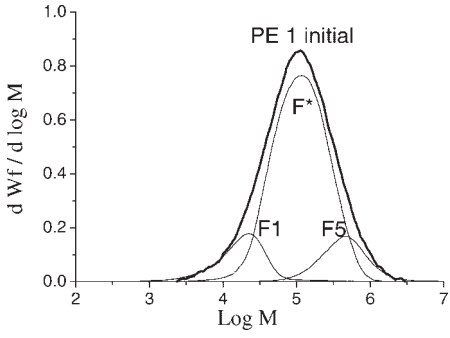

Figure 3.
Data of analysis of MWD of sample 1 as sum of fractions F1; F* and F5 (F* = F2 + F3 + F4; Figure 2, Table 2 and 3).

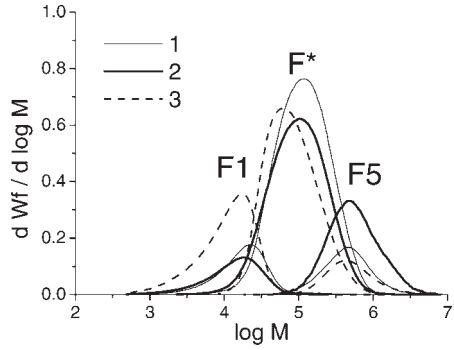

Figure 4.
MWD data of PE samples 1, 2 and 3 as sum of fractions F1; F* and F5 (Table 3).

produces high molecular weight fraction F5, but TMC-5 contains twice higher amount of these centers.

Increasing of hydrogen concentration leads to shift of F^* fraction position for sample 3 toward lower MW in comparison with F^* fraction for sample 2, but relative amounts of these fractions are the same for both samples.

This result differs from Maschio's data[5] who found that experimental MWD curve might be extrapolated with three narrow distributions with the same positions of peak maxima independent of hydrogen concentration; increasing of hydrogen concentration leads only to changing of relative amounts of each group of centers in the total polymer. In our case the position (peak maxima) of F1 and F5 are the same for both samples 2 and 3, but relative amounts of these fractions in the total polymer change (F5 decreases from 27% for sample 2 to 9% for sample 3; F1 increases from 11% for sample 2 to 29% for sample 3).

It seems that increasing of hydrogen concentration leads to decreasing of the fraction of centers which produce the higher molecular weight PE but these centers are not reactive in chain transfer reaction with hydrogen because peak maxima on MWD curve for this fraction stay constant. We have observed the similar phenomena but in much more scale at the study of ethylene polymerization over vanadium-magnesium catalysts.[9]

Thus in the present study we propose a new approach for MWD curve analysis based on the experimental fractionation results. It was shown that experimental MWD curve for PE produced over TMC might be extrapolated with three fractions associated with three groups of active centers. Broadening of MWD of PE with increasing of Ti content in the catalyst is caused by higher amount of centers which produce PE with higher MW. Increasing of hydrogen concentration leads to shifting of central peak maxima and increasing of relative amount of centers which produce PE with lower MW. The understanding of the nature of these centers is the goal of our following work.

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