Study of Multi-Site Nature of Supported Ziegler-Natta Catalysts in Ethylene-Hexene-1 Copolymerization

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Summary: Heterogeneity of active centers (AC) of titanium-magnesium catalysts (TMC) and vanadium-magnesium catalyst (VMC) in ethylene-hexene-1 copolymerization has been studied on the base of data of polymer molecular weight distribution (MWD) deconvolution technique and copolymer fractionation onto narrow fractions. It was found that 3 and 4 Flory components (groups of active centers) are required to describe experimental MWD curves of copolymers produced over TMC with different Ti content. In the case of VMC MWD of homopolymer and copolymer are characterized by set of 5 Flory components (5 groups of AC).
Different character of inter-relationship between MW and short chain branching (SCB) was found for ethylene-hexene-1 copolymers produced over different catalysts: heterogeneous type in the case of TMC and more uniform for copolymer prepared over VMC. The content of Ti affects on the slope of that profile in copolymers produced over TMC.
The results indicated that TMC and VMC are different greatly on the heterogeneity of active centers to the formation of polymers with different molecular weights and to formation of copolymers with different inter-relationship between MW and short chain branching. TMC produces polymers with more narrow MWD but it contains highly heterogeneous centers regarding comonomer reactivity ratios. VMC produces polymers with broad and bimodal MWD but it contains more homogeneous centers regarding comonomer reactivity ratios.

Keywords: ethylene-hexene-1 copolymerization; molecular weight distribution; polyethylene (PE); Ziegler-Natta polymerization

Introduction

It is well known that rheological and mechanical properties of polymers depend not only on their average molecular weights and composition (the content branching), but also on their molecular weight distribution (MWD) and short chain branching (SCB) distribution.[1,2]

The importance of control SCB distribution is illustrated for high density polyethylene used for pipe applications.[3,4] These polymers show exceptionally good resistance to environmental stress cracking, resistance to rapid crack propagation and creep resistance. The key criterion for this application is to produce polymers with bimodal MWD where the short chain branches are concentrated in the high molecular weight fraction of the distribution and serve as tie molecules. Common method to tailor molecular weight distribution and short chain branching distribution typically include tandem or cascade reactors that produce the desired polymer depending on the polymerization conditions in each reactor.

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Another method for tailoring of short chain branching distribution in copolymer is catalyst design. Such approach was used for metallocene catalysts[5,6] and Cr based catalyst.[1] Supported Ziegler Natta catalysts usually produce copolymers in which comonomer is concentrated mainly in low molecular weight part.[7–10]

In our previous papers, we have demonstrated the possible ways of MWD control for polyethylene (PE) by variation of transition metal compound in $MgCl_2$-supported Ziegler Natta catalysts.[11–13] MWD of PE, produced over titanium-magnesium catalyst (TMC) is narrow or medium, depending on Ti content in the catalyst ($M_w/M_n = 3.1–4.8$).[14] Vanadium-magnesium catalyst (VMC) produces PE with broad and bimodal MWD ($M_w/M_n = 12–21$).[11]

For detailed MWD analysis we used deconvolution of experimental MWD curves of polymers on the several Flory components. This method of analysis of the heterogeneity of active centers in Ti based Ziegler-Natta catalysts is widely used in the literature.[9,10,15–17] Discrepancy measure between the resulting MWD (obtained by sum of all Flory components) and initial experimental MWD curve is one of the main issues being discussed. Soares and Hamielec[15] proposed to increase the number of Flory components until the sum of the squares of the residuals (difference between experimental MWD and theoretical fitting) does not improve significantly by adding another site type. We consider that they use very thorough fitting (much more precise than MWD measurement experimental error). Using this approach, they have found six Flory components for polymer with polydispersity of 4.3. In further work, Soares[18] proposed to use additional variance σ^2 in Flory function. This procedure allows to decrease the number of Flory functions needed, and as a result, the number of groups of active centers in the catalyst. It was shown that using suitable σ^2 value permits to use even one site type for describing of MWD of PE produced over Ziegler–Natta catalyst and thus using variance in calculation should be very careful. Soares propose to use multivariable parameter estimation techniques for adequate describing of the number of active centers in Ziegler –Natta catalysts (not only MWD deconvolution but 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 used in.[16]

In our work, we used Kissin's approach of fitting experimental MWD curves with minimum set of Flory components with accuracy about 1–1.5% in standard deviation value.[19] We have assumed that the number of active sites for each catalytic system is equal to the number of Flory components.

Kissin with coworkers[9,17] has found that four-five Flory components are often needed to adequately describe 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. They found that hydrogen reduces catalyst activity and decreases molecular weight (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, they found that introducing hexene-1 leads to increase in contribution of lower molecular weight centers while all peak positions of Flory components stay the same.

In the present article heterogeneity of active centers of TMC and VMC has been studied and discussed on the base of polymer MWD deconvolution technique and copolymer fractionation onto narrow fractions. The new results about more uniform comonomer distribution across molecular weight in ethylene-hexene-1 copolymers produced over supported vanadium-magnezium catalysts were demonstrated.

Experimental Part

Catalysts

Supported catalysts TMC-0.1 and TMC-5 (content of Ti is 0.1 and 5 wt% correspondingly) and VMC (1.7 wt% of V) were obtained via the procedure described elsewhere[11,14,20] by supporting $TiCl_4$ (TMC) or VCl_4 (VMC) on highly dispersed magnesium dichloride with average particle size 10 μm and narrow particle size distribution.

Slurry copolymerization of ethylene with hexene-1 was performed in a 0.8 L steel reactor, in heptane, at constant ethylene pressure and polymerization temperature 80 °C; triisobutylaluminum (TIBA) was used as a co-catalyst, its concentration being 6 mmol TIBA/l, catalyst concentration was 0.04 g/L. Hydrogen was used as a chain transfer agent to control MW of PE. Hexene-1 was added in the reactor at the beginning of the experiment. Copolymerization time (the yield of copolymer) was chosen so that the change in hexene-1 concentration in the reaction medium did not exceed 10–15 wt. %. The pressure was kept constant due to continuous feed of ethylene in the reactor.

MWD measurements were performed using a PL 220 Gel Permeation Chromatograph. Run conditions were as follows: temperature 160 °C; 1,2,4-trichlorobenzene (TCB) was used as a solvent with a flow rate of 1 cm^3/min. Four mixed bed TSK-gel columns (GMHXL-HT, Tosoh Corp.) were used. Universal calibrations ($\log\{MW \times [\eta]\}$ vs. retention volume) were made using narrow Polystyrene standards and PE standards.

Deconvolution of MWD curves was performed based on approach described elsewhere.[15,16,19] It was assumed that in multisite catalysts each type of active centers produces 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:

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

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 molecular weight distribution corresponds to Mw/Mn = 2.

The overall molecular weight distribution of the polymer (composed of the individual Flory components) is therefore:

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

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

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

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

where $q^{exp}(n)$ is 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 – sum of all Flory components in point i, W_{exp} – experimental value of MWD distribution in point i.

An example of good fitting of calculated and experimental MWD curves for copolymers produced over TMC and VMC is shown on the Figure 1.

Fractionation of polymers was performed using automated PolymerChar fractionation station PREP mc^2 according to molecular weight (liquid-liquid fractionation): 1 g of the sample was dissolved in 200 ml of xylene at 130 °C during 2 hours. Then calculated amount of diethylene glycol monobutyl ether was added, and a part of polymer precipitated. Hot solution of polymer was filtered to collecting bottle. Precipitated polymer was dissolved again in xylene and this procedure of dissolving and precipitating was repeated in order to

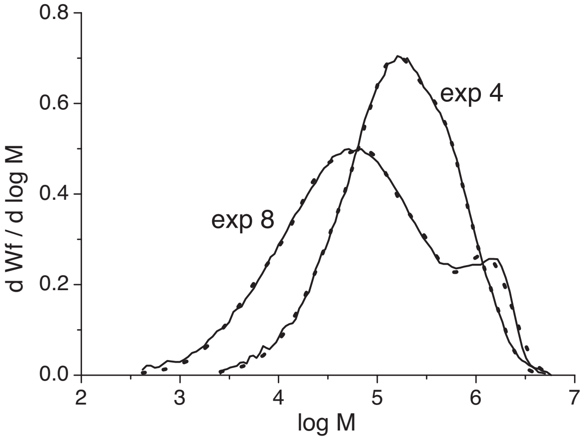

Figure 1.

The experimental (solid lines) and calculated (dash lines) MWD curves for polymers produced over TMC (exp 4) and VMC (exp 8). Experiment numbers correspond to those in Table 1.

obtain 5–6 fractions with Mw/Mn ≤ 2. The last fraction was removed from dissolution vessel as a solution in xylene.

Comonomer content in copolymers and fractions was determined by IR and ^{13}C NMR, as described earlier.[21,22]

Melting temperature and crystallinity of the polymer was determined by means of differential scanning calorimetry (DSC) using NETSCH DSC 204 F1 equipment, according to ASTM D3418-82 procedure. Data on the second melting is represented in Table 1.

Results and Discussion

Influence of Catalyst Composition on MWD of Ethylene-hexene-1 Copolymers

Earlier we have presented the preliminary results on the effect of hexene-1 on MWD of copolymers produced over TMC and VMC.[13] In present study two TMC samples with Ti content of 0.1 wt.% (TMC-0.1) and 5 wt/% (TMC-5) and VMC sample (1.7 wt/% of V) were used. Data on the ethylene-hexene-1 copolymerization over these catalysts, and copolymer characteristics are presented in Table 1.

Table 1.

Data on ethylene-hexene-1 copolymerization over TMC and VMC and characteristics of polymers produced.

Catalyst	Exp. N	[C6]/[C2]1)	Activity, Kg PE/g Ti (V) × h × bar C2H4	C_6H_{12} 2) (mol%)	Mw, $\times 10^{-3}$	Mw/Mn	Mz/Mw	Tm, °S	X, %
TMC-0.1 3)	1	–	450	–	310	3.3	2.6	139.0	67.8
	2	2.7	1020	2.2	220	3.5	2.7	125.8	37.9
	3	4.1	610	3.0	170	4.0	2.7	125.9	37.2
TMC-5 3)	4	–	33	-	330	4.9	2.8	138.1	67.9
	5	2.6	130	1.3	220	4.3	2.6	128.4	47.2
	6	5.2	200	4.1	150	4.0	2.8	126.1	33.2
VMC 4)	7	–	28	–	390	18	3.3	136.3	64.5
	8	0.39	59	1.1	320	18	4.4	128.7	54.6

1) Comonomer concentration ratio in heptane;

2) Hexene-1 content in copolymer.

3) Ethylene pressure 2 bar; $[H_2]/[C_2H_4] = 0.13$ in gas phase;

4) Ethylene pressure 7 bar; $[H_2]/[C_2H_4] = 0.07$ in gas phase.

VMC has much higher ability to copolymerize α-olefins with ethylene (the lower comonomer reactivity ratio - r_1 value) comparing to TMC,[23,24] and higher reactivity in chain transfer reaction with hydrogen[11,25] as well. Therefore in order to obtain copolymers with Mw range of **2** $^*10^5$–4 $^*10^5$, containing 1.1–4.1 mol.-% of hexene-1, the lower $[C_6H_{12}]/[C_2H_4]$ and $[H_2]/[C_2H_4]$ ratios in reaction medium are required at copolymerization over VMC in comparison with copolymerization over TMC.

Data presented in Table 1 (exps. 1–6) show the Mw/Mn values of copolymers produced over TMC catalysts changes slightly in comparison with homopolymers. Introduction of hexene-1 during polymerization over VMC causes certain MWD broadening (Figure 4): the main MWD peak is shifted to low MW region while the high MW shoulder stays at the same position. As a result, Mz/Mw value increases from 3.3 up to 4.4. Mw/Mn values do not change because of simultaneous decreasing of Mw and Mn values.

The thermal characteristics of the polymers examined are represented as well in Table 1. It is seen the values of melting temperature and crystallinity of homopolymer, produced over VMC, are lower than those for TMC (Table 1, exps. 1, 4 and 7). It is probably associated with presence of small amount of methyl branches in PE produced over VMC. The presence of methyl branches was shown in our previous work.[22] Intramolecular isomerization of the growing polymer chain seems to be a possible reason for the formation of methyl branches.[22]

We have studied the heterogeneity of active centers of TMC and VMC at copolymerization of ethylene with hexene-1 in detail, using deconvolution of MWD curves of copolymers on the Flory components and by measuring the content of short chain branching in the narrow fractions after fractionation of copolymers. The results of deconvolution of experimental MWD curves into Flory components of homopolymers and copolymers produced over TMC and VMC are shown in Figure 2–4 and Table 2 and 3.

In the case of polymerization over TMC-0.1 catalyst three Flory components are sufficient (Figure 2 and Table 2, exps. 1, 2, 3). In the case of polymerization over TMC-5 catalyst, MWD of homo- and copolymers are characterized by set of four Flory components (Figure 3 and Table 2, exps. 4, 5, 6). Introducing of hexene-1 in ethylene polymerization over TMC-5 and TMC-0.1 catalysts leads to the shift of all Flory components towards lower molecular

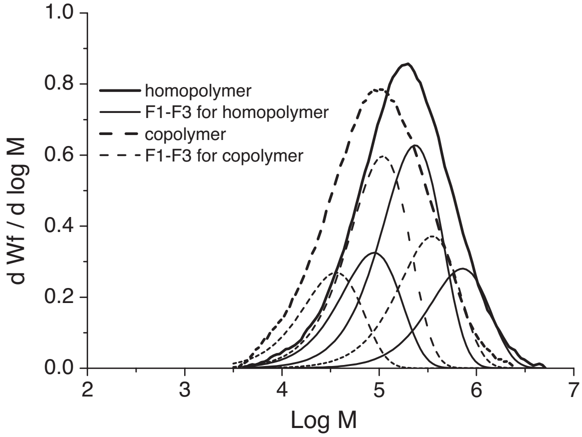

Figure 2.
The results of MWD curves deconvolution into Flory components of homo- and copolymer produced over TMC-0.1 (exps. 1 and 3 in Table 1).

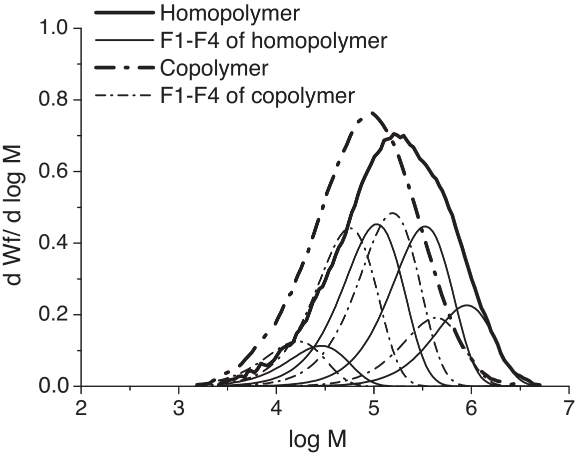

Figure 3.
The results of MWD curves deconvolution into Flory components of homo- and copolymer produced over TMC-5 (exps. 4 and 6 in Table 1).

weight region. It means that all types of TMC active centers are active in chain transfer reaction with comonomer. The contribution of Flory components to MWD for homo- and copolymers is similar (Table 2). This result differs from data obtained by Kissin and co-workers.[9] According to them, introduction of hexene-1 in polymerization reduces relative content of polymer, produced by high MW-polymeric sites, practically with no change in positions of all Flory components. Such difference in copolymerization data, along with dissimilarities in reaction of chain transfer reaction with hydrogen, can be explained by difference in catalyst composition.

In the case of VMC MWD of homo- and copolymer are be characterized by set of five Flory components (Table 3, Figure 4).

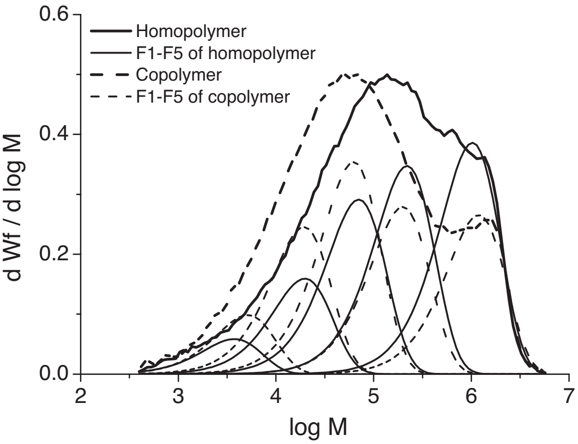

Figure 4.
The results of MWD curves deconvolution into Flory components of homo- and copolymer produced over VMC (exps. 7 and 8 in Table 1).

Table 2.
The results of MWD curves deconvolution into Flory components of homo- and copolymer produced over TMC-0.1 and TMC-5 (experiment numbers correspond to Table 1).

Exp N	1		2			3			4		5		6		
Flory component	Fraction weight, %	Mw × 10^{-3}	Fraction weight, %	Mw × 10^{-3}	r_1	Fraction weight, %	Mw × 10^{-3}	r_1	Fraction weight, %	Mw × 10^{-3}	Fraction weight, %	Mw × 10^{-3}	Fraction weight, %	Mw × 10^{-3}	r_1
I	–	–	–	–	–	–	–	–	9.1	29	9.4	28	10.1	17	65
II	26.1	89	26.6	58	85	21.6	36	100	36.4	107	41.1	94	35.5	57	130
III	50.4	234	46.9	156	140	47.9	109	150	35.9	336	36.1	257	38.9	156	240
IV	22.5	718	25.5	489	280	29.8	350	300	18.2	900	12.6	650	15.4	433	420
Sum															
Mw ×10^{-3}	310		220			170			330		220		148		
Mw/Mn	3.3		3.5			4.0			4.7		4.3		4.0		

Practically all peaks of Flory component stay at the same position. Changing of copolymer MWD is the result of increasing contribution of components with low MW and decreasing contribution of components with higher MW.

Influence of Catalyst Composition on Active site Heterogeneity in Ethylene-hexene-1 Copolymerization (Compositional Heterogeneity)

To examine compositional heterogeneity of copolymers, produced over TMC and VMC and accordingly heterogeneity of active sites of these catalysts in ethylene-hexene-1 copolymerization we carried out the fractionation of the polymers into narrow fractions (with Mw/Mn = 1.4–2.5) with subsequent analysis of hexene-1 content of separate fractions.

According to data on comonomer content in each fraction the profile of inter-relationship between MW and short chain branching content, was constructed. An example of the profile for copolymer 2 in Table 1 produced over TMC-0.1 is presented in Figure 5. It is seen that branching content decreases with increasing of Mw of polymer fractions. Profiles of inter-relationship between MW and SCB content for copolymers produced over TMC with various Ti content is presented in Figure 6. It is seen that a heavy concentration of branching in the lowest MW is observed for the copolymer produced over TMC-5 (amounts of butyl branching in the first and the last fractions differ approximately five-fold). High heterogeneity of SCB content in copolymers obtained over TMC was shown in the literature.[7–10] Soares and co-workers[7,8] measured profiles of SCB versus MW in ethylene-hexene-1 copolymer obtained over TMC (product of chlorination of $Ti(OBu)_4$ and $Mg(OEt)_2$ with $AlEt_2Cl$) using analysis of high temperature gel-permeation

Table 3.
The results of MWD curves deconvolution into Flory components of homo- and copolymer produced over VMC (experiment numbers correspond to Table 1).

Exp N	7		8		
Flory component	Fraction weight, %	Mw ×10^{-3}	Fraction weight, %	Mw ×10^{-3}	r_1
I	4.7	3.9	7.9	5	32
II	12.8	20	19.7	19	34
III	23.4	70	28.4	62	36
IV	27.9	220	22.4	198	39
V	31.0	1020	21.3	1180	40
Sum					
Mw ×10^{-3}	400		300		
Mw/Mn	16.9		18		

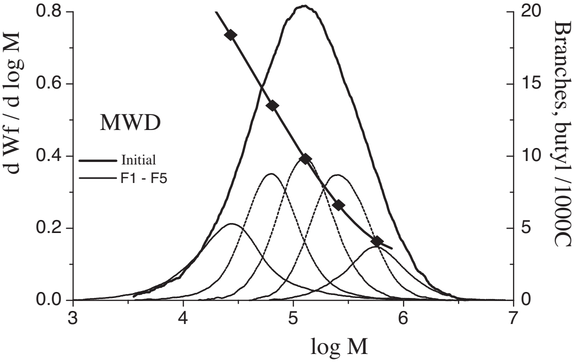

Figure 5.
Data on ethylene-hexene-1 copolymer fractionation into five fractions for determination of the inter-relationship between MW and short chain branching (exp. 2 in Table 1).

chromatography fractions with Fourier-transform infrared spectroscopy. They shown comonomer is concentrated in the lower molecular weight part of polymer. Later Kissin for $TiCl_4/Mg(OEt)_2/SiO_2$ catalyst[9] and Zhang for $TiCl_4/MgCl_2$ catalysts (product of reaction of $MgCl_2{}^*EtOH$ with $TiCl_4$)[10] have also demonstrated that most part of comonomer (hexene-1) is concentrated in the lower molecular weight part of copolymers.

We have found decreasing of the titanium content in catalyst leads to decrease in inclination angle of profiles of inter-relationship between MW and short chain branching, but in general, the distribution has still skew profile (amounts of butyl branching in the first and the last fractions differ approximately three-fold for TMC-0.1) (Figure 6).

Very different almost flat branch profile was found for copolymer produced over VMC (Figure 7, line 8). Comparative data on MWDs and the inter-relationship between MW and SCB for copolymers produced over TMC and VMC are represented in Figure 7. It is seen that branch profiles vary from highly concentrated in the low MW part for TMC to uniformly distributed over all of MW range for VMC.

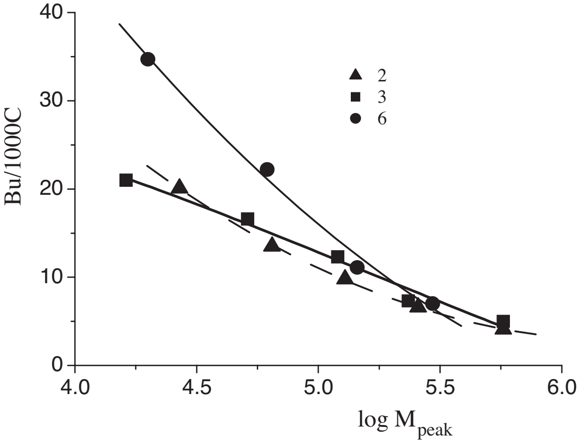

Figure 6.
Profiles of inter-relationship between MW and short chain branching for copolymers obtained over TMC-0.1 (exps. 2 and 3) and TMC-5 (exp 6). Experiment numbers correspond to Table 1.

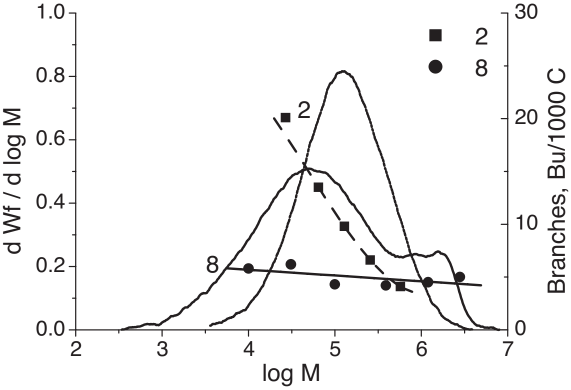

Figure 7.
Comparison of MWD and the inter-relationship between MW and short chain branching for copolymers obtained over TMC-0.1 and VMC (exps. 2and 8 in Table 1).

Hereby replacement of $TiCl_4$ by VCl_4 leads not only to broad bimodal MWD of copolymer, but to more uniform profile of the inter-relationship between MW and short chain branching as well.

Comonomer reactivity ratios (r_1 values) for different groups of active centers, which correspond to individual Flory components have been estimated using the data on branching content in different fractions and MWD curve deconvolution into Flory components (Tabs. 2 and 3). As example the data used for calculation of r_1 values for different groups of active centers are presented in Figure 8. The profile of SCB and MWD curve deconvolution into Flory components are overlapped and comonomer content corresponding to maximum of Flory component (at point of crossing of SCB profile and maximum of Flory component) was determined as value $(C_6H_{12}/C_2H_4)_{pol}$. Then r_1 values were calculated using the equation (5):

$$(C_6H_{12}/C_2H_4)_{pol.} = 1/r_1\ [C_6H_{12}/C_2H_4] \qquad (5)$$

were $[C_6H_{12}/C_2H_4]$ is comonomer molar ratio in reaction medium (data from Table 1).

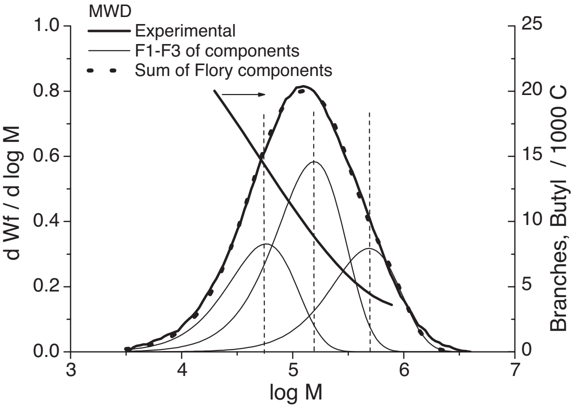

Figure 8.
The data on the MWD curve deconvolution into Flory components and the profile of average SCB content measured for separate fractions of copolymer produced over TMC-0.1 (exp. 2 in Table 1).

Such estimation allows obtaining data on comonomer reactivity ratios (r_1 values) of each group of active sites of TMC and VMC. It can be seen from Table 2 (exp. 4–6) that TMC-5, combines the additional site group which produces low-molecular weight polymer. This active site group possesses higher ability to copolymerize hexene-1 with ethylene ($r_1 = 65$) and TMC-5 produces the more heterogeneous polymer comparing to TMC-0.1. In the case of VMC r_1 values are much lower than they are for TMC (Table 3). Moreover the differences in r_1 values for various active site groups of VMC are lower, than those for TMC. Hence under the same polymerization conditions more homogeneous ethylene-hexene-1 copolymers are produced over VMC than it is in case of TMC.

Hereby TMC and VMC contain heterogeneous active sites in both propagation and chain transfer reaction and incorporation of α-olefins but heterogeneity of the active centers being different for different reactions:

- TMC contains more homogeneous centers at propagation and chain transfer reactions, but these active centers are highly heterogeneous regarding comonomer reactivity ratios.
- VMC contains more heterogeneous centers at propagation and chain transfer reactions and produces polymer with broad MWD, but these centers are more homogeneous regarding comonomer reactivity ratios. So VMC permits to obtain copolymers with broad bimodal MWD and more uniform inter-relationship between MW and short chain branching.

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