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Polymer 42 (2001) 2289–2297

polymer

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Microstructure of ethylene-1-hexene and ethylene-1-octene copolymers obtained over Ziegler–Natta catalysts supported on $MgCl_2(THF)_2$

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Received 30 May 2000; received in revised form 17 July 2000; accepted 20 August 2000

Abstract

The ethylene copolymerizations with 1-hexene or 1-octene in the presence of hydrogen using three catalysts, $MgCl_2(THF)_2/VOCl_3/Et_2AlCl$, $MgCl_2(THF)_2/VCl_4/Et_2AlCl$, $MgCl_2(THF)_2/TiCl_4/Et_2AlCl$, were investigated. It was found that the addition of hydrogen into the copolymerization feed reduces the molecular weight of the copolymers produced and decreases the activity of all the studied catalysts. The microstructure of the copolymers obtained was determined on the basis of ^{13}C NMR investigations and the reactivity ratios of the comonomers were calculated. The lack of tendency of the olefin comonomers to the creation of the polymer block was confirmed. It was found that the products of the comonomers reactivity ratios are close to the value of 1 and they are independent of both the catalyst and comonomer type. This means that the structure of all the copolymers obtained is random. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Copolymerization of ethylene with α-olefin; Microstructure of copolymers; Ziegler–Natta catalysts

1. Introduction

Linear low-density polyethylenes (LLDPE) are linear polyethylenes containing a small amount of short chain branching along the chains due to the insertion of α-olefin units during the polymerization of ethylene. Introduction of the longer α-olefin to the polyethylene chain leads to the decrease of the regularity in the chain structure, and in consequence to lower crystallinity, melting point and density. Therefore, such copolymers have properties that differ from the ones of homopolyethylene. The modification of the properties of polyethylene through copolymerization has great practical importance. The fraction of polyethylenes sold as a true homopolymer, is relatively small, being about 35% [1]. This is the reason why the interest in LLDPE constantly increases. In recent years, many reports concerning ethylene copolymerization with linear alkenes were published [2–27]. The effect of the kind and concentration of the comonomer in the feed on the activity of the catalyst systems, the effect of the kind and structure of the catalyst on its copolymerization activity, the ability of comonomer incorporation, and the properties of the product obtained are commonly studied. It is also known that the kind of the catalyst used for copolymerization has considerable effect on the microstructure of the macromolecules of the products. Most of the published reports concern the copolymerization of ethylene with α-olefins over catalysts having titanium compounds and metallocene systems.

Although considerably less interest is focused in the literature on vanadium-based catalysts, it is known that these catalytic systems are commercially used in the synthesis of EPDM copolymers. Earlier, we found that two vanadium-based catalysts supported on complex magnesium chloride, $MgCl_2(THF)_2VOCl_3/Et_2AlCl$ and $MgCl_2(THF)_2/VCl_4/Et_2AlCl$, offer high activity and stability in ethylene polymerization [28,29].

The results mentioned above motivated us to investigate the properties of these catalysts for the copolymerization of ethylene with α-olefins. In our previous work [30,31] we have reported the results of the comparison of the copolymerization of ethylene with linear α-olefins from 1-pentene to 1-dodecene using vanadium catalysts or titanium catalyst supported on complex magnesium chloride. We showed the effect of the catalyst type, as well as the comonomer type and concentration in the feed on catalytic activity, incorporation of the comonomer, and selected properties of the products obtained. Unfortunately, the determination of the microstructure of the copolymers obtained was unsuccessful. Because of ultra-high molecular weight and consequently very low solubility of the copolymers, made with all investigated catalysts, our attempts to obtain ^{13}C NMR

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PII: S0032-3861(00)00621-2

Table 1
Effect of hydrogen on the catalysts activity in copolymerization of ethylene with 1-hexene or 1-octene

Comonomer type	Without hydrogen[a]		With hydrogen	
	Comonomer concentration (mol/dm^3)	Catalyst activity (kg/mol$_{V(Ti)}$)	Comonomer concentration (mol/dm^3)	Catalyst activity (kg/mol$_{V(Ti)}$)
$MgCl_2(THF)_2/VOCl_3/Et_2AlCl$				
1-Octene	0.091	8663	0.344	367
$MgCl_2(THF)_2/VCl_3/Et_2AlCl$				
1-Hexene	0.113	8471	0.432	397
1-Octene	0.091	8290	0.344	392
$MgCl_2(THF)_2/TiCl_4/Et_2AlCl$				
1-Octene	0.090	1060	0.344	201

[a] $t = 60$ min.

spectra failed. Therefore, to study the effect of the catalytic system on the microstructure of the copolymers we have to reduce the molecular weight of the copolymers. For this purpose the study of the copolymerization was carried out in the presence of hydrogen.

In this work, we present the comparative studies of the copolymerization of ethylene with 1-hexene or 1-octene performed in the presence of hydrogen using vanadium ($VOCl_3$ or VCl_4) and titanium ($TiCl_4$) catalytic systems supported on $MgCl_2(THF)_2$ and activated by Et_2AlCl.

2. Experimental

The materials employed, synthesis of the catalysts, and the ethylene-α-olefin copolymerization procedures adopted were specified in our previous papers [30,31]. When the copolymerization was carried out in the presence of hydrogen this reagent was charged into the reactor before ethylene. The copolymerization conditions were (values in brackets for copolymerization over titanium catalyst): $[V] = 5 \times 10^{-5}$ mol/dm^3 (9×10^{-5} mol/dm^3); $[A] = 25 \times 10^{-3}$ mol/dm^3 (60×10^{-3} mol/dm^3); $p_{Et} = 0.5$ MPa; $p_{H_2} = 0.1$ MPa; $T = 33°C$ (50°C); $t = 30$ min.

2.1. Characterization of the polymers

The molecular weights of the produced polymers were determined by gel permeation chromatography (GPC) with a Waters instrument, model 150-C. The operating conditions of the GPC method were described in Ref. [32]. The molecular weight distributions (MWDs) and the average molecular weights were determined using the universal calibration curve obtained with narrow MWD polystyrene standards.

The ^{13}C NMR spectra of the polymers were recorded

Table 2
Effect of hydrogen on the molecular weight and molecular weight distribution of ethylene/1-hexene and ethylene/1-octene copolymers obtained with the investigated catalysts

Comonomer		$\bar{M}_{n,t} \times 10^{-3}$ (g/mol)	$\bar{M}_{w,t} \times 10^{-3}$ (g/mol)	$\bar{M}_{v,t} \times 10^{-3}$ (g/mol)	$\bar{M}_w/\bar{M}_n$
Type	Concentration (mol/dm^3)				
$MgCl_2(THF)_2/VOCl_3/Et_2AlCl$					
1-Hexene	0.432	22.8	164.5	126.7	7.2
	0.820	19.4	157.4	118.4	8.1
1-Octene	0.344	29.0	252.6	180.7	8.7
$MgCl_2(THF)_2/VCl_4/Et_2AlCl$					
1-Hexene	0.432	30.3	253.3	191.1	8.3
1-Octene	0.344	20.2	179.2	128.0	8.8
	0.653	20.7	150.6	116.0	7.3
$MgCl_2(THF)_2/TiCl_4/Et_2AlCl$					
1-Hexene	0.432	236.3	1137.6	862.9	4.8
	0.820	155.1	615.5	506.6	4.0
1-Octene	0.653	276.8	1111.9	912.2	4.0

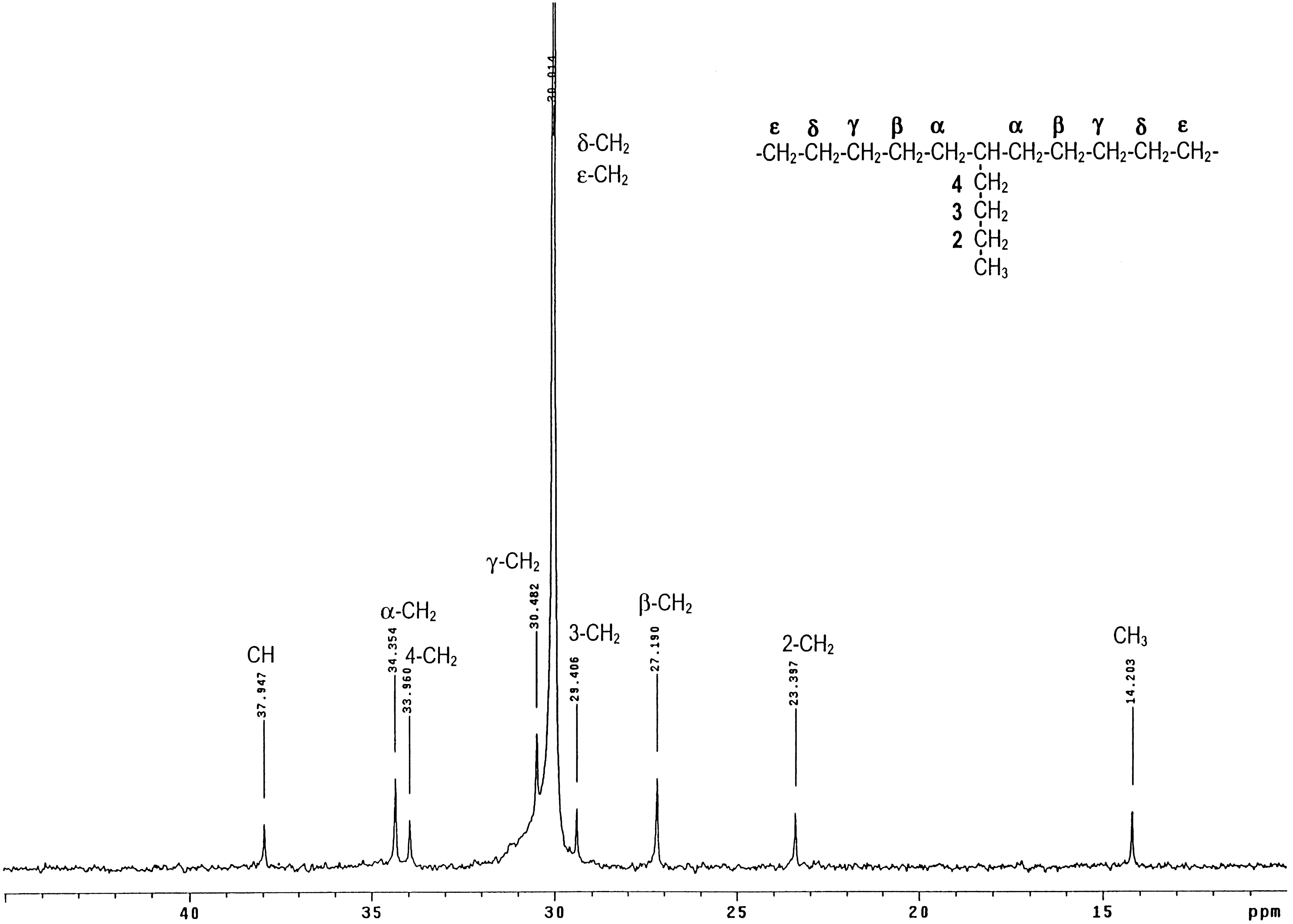

Fig. 1. ^{13}C NMR spectrum of ethylene-1-hexene copolymer.

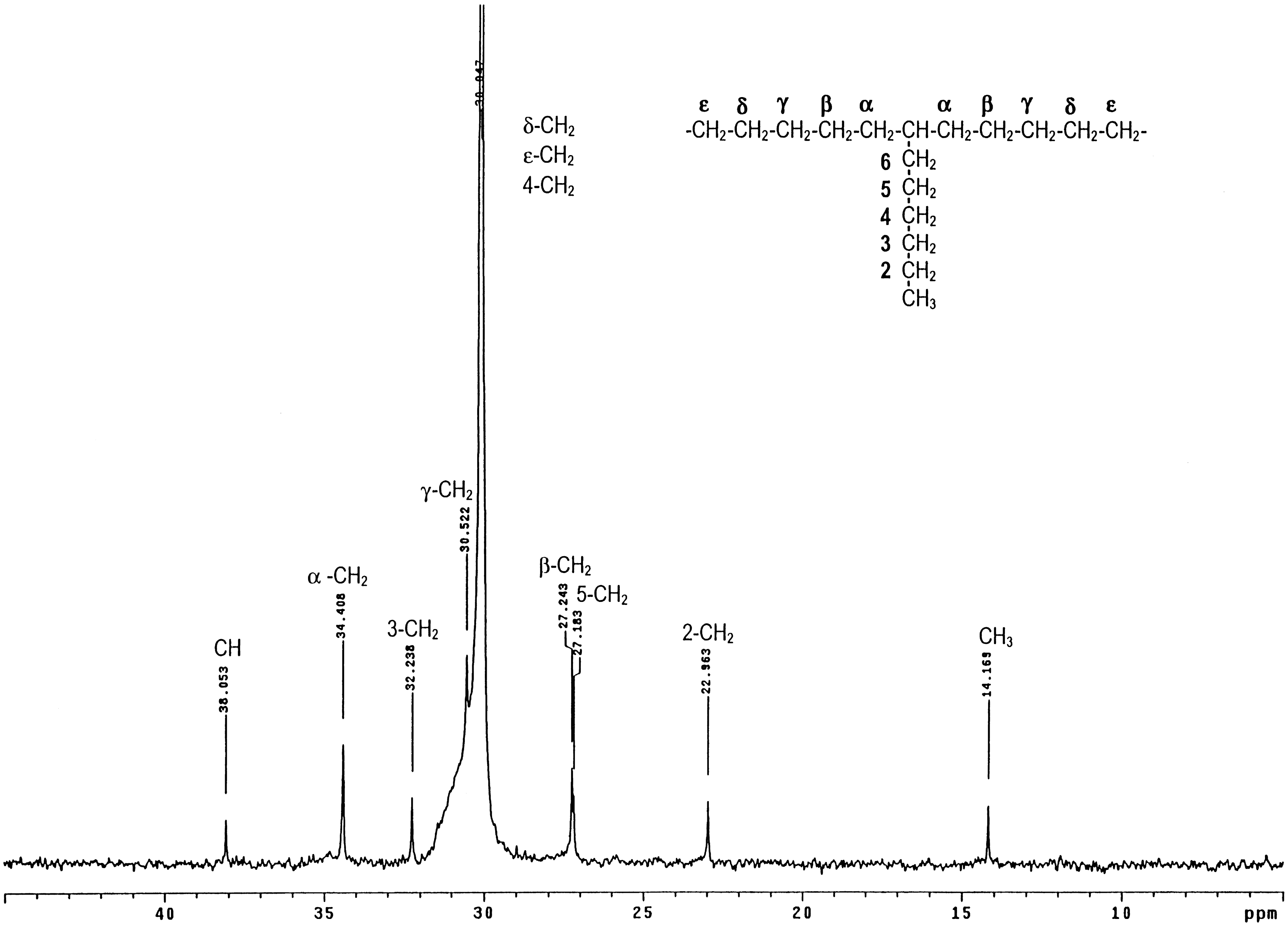

Fig. 2. ^{13}C NMR spectrum of ethylene-1-octene copolymer.

Table 3
Monomer sequence distributions of ethylene/1-hexene copolymers obtained with vanadium and titanium catalysts

	Precursor					
	$VOCl_3$		VCl_4		$TiCl_4$	
	Concentration of 1-hexene in the feed (mol/dm^3)					
	0.432	0.820	0.432	0.820	0.432	0.820
	Triad distribution (mole fraction)					
EHE	0.0136	0.0192	0.0256	0.0299	0.0136	0.0127
EHH	0.0004	0.0008	0.0014	0.0020	0.0004	0.0003
HHH	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HEH	0.0002	0.0004	0.0007	0.0010	0.0002	0.0001
HEE	0.0272	0.0384	0.0512	0.0598	0.0272	0.0254
EEE	0.9586	0.9412	0.9212	0.9070	0.9586	0.9615

Table 4
Monomer sequence distributions of ethylene/1-octene copolymers obtained with vanadium and titanium catalysts

	Precursor					
	$VOCl_3$		VCl_4		$TiCl_4$	
	Concentration of 1-octene in the feed (mol/dm^3)					
	0.344	0.653	0.344	0.653	0.344	0.653
	Triad distribution (mole fraction)					
EOE	0.0146	0.0229	0.0136	0.0238	0.0069	0.0088
EOO	0.0004	0.0010	0.0004	0.0012	0.0000	0.0000
OOO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
OEO	0.0002	0.0005	0.0002	0.0006	0.0000	0.0000
OEE	0.0292	0.0458	0.0272	0.0476	0.0138	0.0177
EEE	0.9557	0.9297	0.9586	0.9269	0.9791	0.9732

at 95°C using a Varian, Unity Inova 300 spectrometer operating at 75 MHz. The samples were dissolved in 1,2,4-trichlorobenzene/benzene-d_6.

The heat of fusion (ΔH_f) and melting temperature (T_m) were measured with the use of a TA Instruments 2010 DSC calorimeter at a heating rate of 5 K/min. From ΔH_f was calculated percent crystallinity using the expression: $X_c = \Delta H_f \cdot (100/290)$ [33].

3. Results and discussion

Table 1 presents the results of the copolymerization of ethylene with 1-hexene or 1-octene over the three studied catalysts and the comparison results of the copolymerization without hydrogen on the same catalytic systems. As can be seen, the introduction of hydrogen to the polymerization reactor depresses the catalyst activity of all the investigated catalytic systems. However, in both series the comonomer concentration was different, but as results from our previous studies showed, the comonomer concentration above a certain value had no effect on the catalyst activity. In addition, these results show that the influence of hydrogen on the catalyst activity depends on the type of the catalyst. The vanadium catalysts are more sensitive to the reduction of their activity by hydrogen than the titanium catalyst. Earlier, the same dependence was observed in case of ethylene polymerization [34].

Also, it was found (Table 2) that the introduction of hydrogen into the ethylene copolymerization process with longer α-olefins leads to considerable and expected decrease of the molecular weight of the copolymers obtained. The effect of hydrogen on the molecular weight of the copolymers over different studied catalytic systems is similar to that obtained for polyethylene. The decrease of the molecular weight of the copolymers is similar for both

Table 5
Structural parameters characterizing the ethylene/1-hexene copolymers

Structural parameters	Precursor					
	$VOCl_3$		VCl_4		$TiCl_4$	
	1-Hexene concentration in the feed (mol/dm^3)					
	0.432	0.820	0.432	0.820	0.432	0.820
Mole fraction of 1-hexene: [H]	0.014	0.020	0.027	0.032	0.014	0.013
Mole fraction of ethylene: [E]	0.986	0.980	0.973	0.968	0.986	0.987
Total number of 1-hexene runs per average molecule, [N]	0.0138	0.0196	0.0263	0.0309	0.0138	0.0128
Run number, [RN] (100[N])	1.38	1.96	2.63	3.09	1.38	1.28
Average sequence length of 1-hexene, L_H	1.01	1.02	1.03	1.04	1.01	1.02
Monomer dispersity, [MD]	98.6	98.0	97.4	96.6	98.6	98.5
Average sequence length of ethylene, L_E	71.4	50.0	37.0	31.3	71.4	77.1

Table 6
Structural parameters characterizing the ethylene/1-octene copolymers

Structural parameters	Precursor					
	$VOCl_3$		VCl_4		$TiCl_4$	
	1-Octene concentration in the feed (mol/dm^3)					
	0.344	0.653	0.344	0.653	0.344	0.653
Mole fraction of 1-octene: [O]	0.015	0.024	0.014	0.025	0.007	0.009
Mole fraction of ethylene: [E]	0.985	0.976	0.986	0.975	0.993	0.991
The total number of 1-octene runs per average molecule, [N]	0.0148	0.0234	0.0138	0.0244	0.0069	0.088
Run number, [RN] (100[N])	1.48	2.34	1.38	2.44	0.69	0.88
Average sequence length of 1-octene, L_O	1.01	1.02	1.01	1.03	1.01	1.02
Monomer dispersity, [MD]	98.7	97.5	98.6	97.6	98.6	97.8
Average sequence length of ethylene, L_E	66.6	41.7	71.5	40.0	143.9	112.6

Table 7
The reactivity ratios of the studied monomer pairs

Comonomer type	r_E	r_C	$r_E r_C$
$MgCl_2(THF)_2/VOCl_3/Et_2AlCl$			
1-Hexene	49.00	0.0204	1.00
1-Octene	53.16	0.0173	0.92
$MgCl_2(THF)_2/VCl_4/Et_2AlCl$			
1-Hexene	33.15	0.0294	0.97
1-Octene	54.71	0.0196	1.07
$MgCl_2(THF)_2/TiCl_4/Et_2AlCl$			
1-Hexene	74.18	0.0129	0.96
1-Octene	125.99	–	–

vanadium catalysts [to the level $\bar{M}_v = (1–2) \times 10^5$] and much greater in comparison to the titanium system ($\bar{M}_v \approx 1 \times 10^6$). On the other hand, the latter gives products having narrower molecular weight distribution ($\bar{M}_w/\bar{M}_n = 4–5$) in comparison to vanadium catalysts ($\bar{M}_w/\bar{M}_n = 7–9$). The comparison of these properties with the polydispersity index of polyethylene made with the same catalysts [34] reveals that the presence of α-olefin comonomer has no effect on this feature. It can be assumed that the comonomer does not change the active site distribution and probably their chemical nature. However, the molecular weight of the copolymers obtained was found to be dependent on comonomer concentration in the feed. An increase in comonomer concentration causes a decrease in the

Table 8
Properties of the ethylene/1-hexene and ethylene/1-octene copolymers obtained in the presence of hydrogen

Comonomer	Comonomer concentration (mol/dm^3)	Comonomer content (%mol)	Melting point (°C)	Crystallinity (%)
$MgCl_2(THF)_2/VOCl_3/Et_2AlCl$				
–	–	–	141.29	55.7
1-Hexene	0.432	0.014	130.93	49.7
	0.820	0.020	131.92	43.2
1-Octene	0.344	0.015	134.70	50.8
	0.653	0.024	133.75	48.7
$MgCl_2(THF)_2/VCl_4/Et_2AlCl$				
–	–	–	139.01	55.8
1-Hexene	0.432	0.027	130.91	45.7
1-Octene	0.653	0.025	131.76	40.8
$MgCl_2(THF)_2/TiCl_4/Et_2AlCl$				
1-Hexene	0.432	0.014	135.32	41.2
	0.820	0.013	131.20	36.3
1-Octene	0.344	0.007	138.38	46.8
	0.653	0.009	135.30	51.9

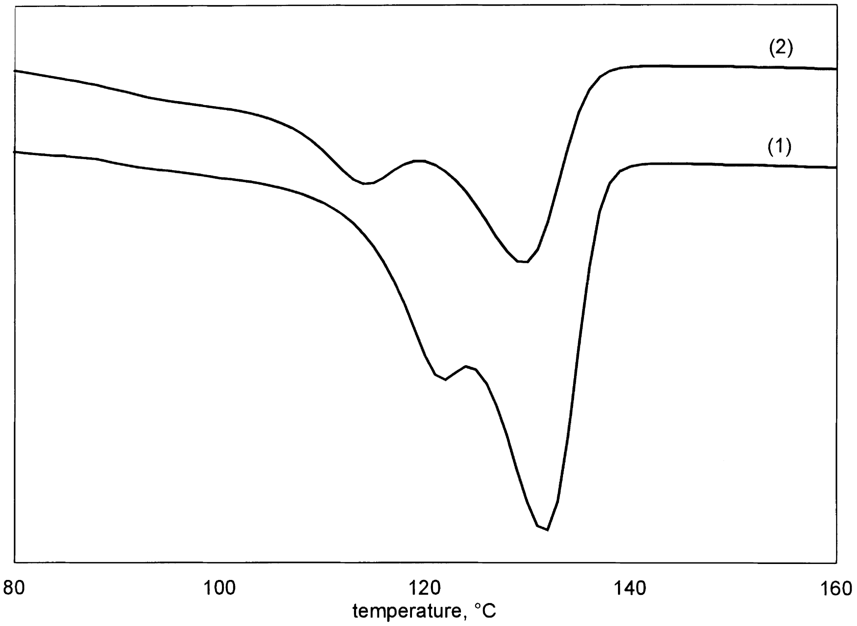

Fig. 3. Thermograms of ethylene/1-hexene copolymers obtained with $MgCl_2(THF)_2/VCl_4/Et_2AlCl$ catalyst and in the presence of hydrogen; concentration of 1-hexene in the feed, mol/dm^3: (1) 0.432; (2) 0.820.

molecular weight of the comonomer. This shows that there is a transfer reaction with the comonomer.

The decrease of the molecular weight of the copolymerization products obtained with the presence of hydrogen causes an increase in their solubility, which makes the ^{13}C NMR analysis of these copolymers possible. Figs. 1 and 2 show typical ^{13}C NMR spectra of the copolymers of ethylene with 1-hexene and 1-octene, respectively.

On the basis of ^{13}C NMR data, the contributions of all possible triads sequences which occur in the copolymers macromolecules were calculated using Bernoullian's statistics. The results are presented in Tables 3 and 4.

Additionally, to determine more precisely the microstructure of the analysed copolymers, the structural parameters characterizing the copolymer chain were calculated using the Randall method [35]. The results of these calculations for 1-hexene and 1-octene comonomers are presented in Tables 5 and 6, respectively.

Although the concentration of the comonomer in the feed was the same for all the investigated catalysts, the results of the calculations show that the copolymers obtained with

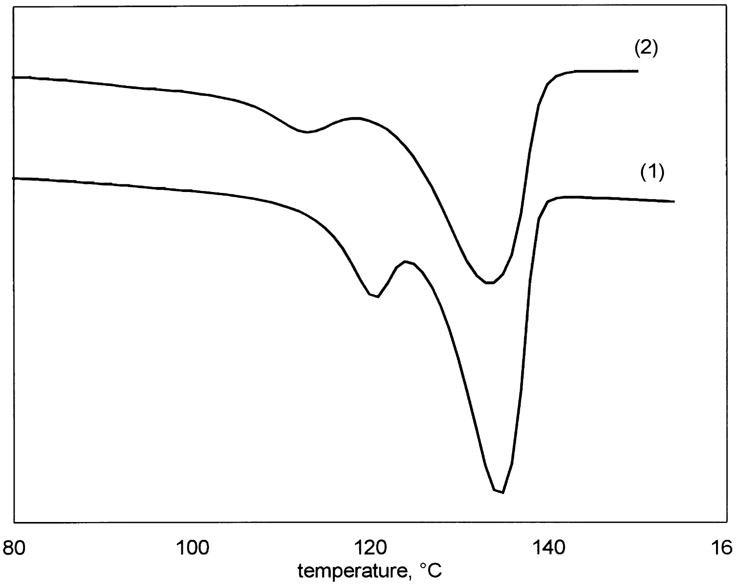

Fig. 4. Thermograms of ethylene/1-octene copolymers obtained with $MgCl_2(THF)_2/VOCl_4/Et_2AlCl$ catalyst and in the presence of hydrogen; concentration of 1-octene in the feed, mol/dm^3: (1) 0.344; (2) 0.653.

both vanadium-based catalysts have a higher contribution of the comonomer in the product than those obtained with the titanium catalyst. Therefore, the incorporation of α-olefins into the polyethylene chain is more effective in case of the vanadium catalysts compared to the titanium catalyst. Also, it can be noticed that in comparison to the titanium catalytic system, the copolymers composition of both vanadium catalysts depends much more on the comonomer concentration in the feed.

On the other hand, the calculated values of monomer dispersity, MD, for almost all copolymerization products are close to the value of 100, and do not depend on the contribution of higher olefin and the kind of catalyst. This means that all or almost all H and O units in the macromolecules are isolated.

On the basis of the sequence of the copolymer composition determined by the ^{13}C NMR method, the apparent reactivity ratios of the comonomers were calculated. For this purpose we used the following equations known from literature [36]:

$$[\mathrm{EE}] = (2[\mathrm{EEE}] + (\mathrm{CEE}])/2 \tag{1}$$

$$[\mathrm{CC}] = (2[\mathrm{CCC}] + (\mathrm{CCE}])/2 \tag{2}$$

$$[\mathrm{EC}] = (2[\mathrm{ECE}] + [\mathrm{CCE}] + [\mathrm{CEE}] + 2[\mathrm{CEC}])/2 \tag{3}$$

$$[\mathrm{E}] = [\mathrm{EE}] + [\mathrm{EC}]/2 \tag{4}$$

$$[\mathrm{C}] = [\mathrm{CC}] + [\mathrm{CE}]/2 \tag{5}$$

$$P_{\mathrm{EE}} = [\mathrm{EE}]/[\mathrm{E}] = 1 - P_{\mathrm{EC}} \tag{6}$$

$$P_{\mathrm{CC}} = [\mathrm{CC}]/[\mathrm{H}] = 1 - P_{\mathrm{CE}} \tag{7}$$

$$r_{\mathrm{E}} = P_{\mathrm{EE}}/P_{\mathrm{EC}} \tag{8}$$

$$r_{\mathrm{C}} = P_{\mathrm{CC}}/P_{\mathrm{CE}} \tag{9}$$

where E is ethylene, C is the longer α-olefin (i.e. 1-hexene or 1-octene), r_{E}, r_{C} the reactivity ratios of ethylene and the longer α-olefin, respectively.

The results presented in Table 7 confirm that vanadium catalysts have higher efficiency in the ethylene copolymerization process with α-olefin than titanium catalyst. Additionally, for all catalyst systems, with the increase of the chain length of the olefin comonomer its ability to copolymerize decreases. The lack of tendency of the olefin comonomers to the creation of the polymer block is also confirmed. It was found that the products of the comonomers reactivity ratios, $r_{\mathrm{E}} \cdot r_{\mathrm{C}}$, are close to the value of 1 and they are independent of both the catalyst and comonomer type. It means that the structure of all the copolymers obtained is random.

3.1. Average properties of the copolymers

The average properties of the copolymers produced in the presence of hydrogen over the catalytic systems studied are shown in Table 8.

As can be seen, the melting temperature and crystallinity of the copolymers are lower than the properties of homopolyethylene obtained in the presence of the same concentration of hydrogen and decrease with the increase of comonomer content in the copolymer. The effect of the copolymers composition on thermal behaviour is also shown in Figs. 3 and 4. We can observe a decrease of the melting point and broadening of the curve shape as a result of higher α-olefin content in the copolymer.

It should be stressed that the DSC curves obtained in the standard method (Figs. 3 and 4) had more than one endothermic peak. Additionally, these peaks showed the broadening of the curve shape for the copolymers having higher comonomer contribution. Therefore, our investigations were focused on the determination of the effect of both comonomers and particularly catalyst type on the copolymer composition distribution.

Acknowledgements

This work was financially supported in part by the State Committee for Scientific Research of Poland.

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