

Pietikäinen, P., Seppälä, J.V., Ahjopalo, L., and Pietilä, L.-O., Copolymerization of Ethylene and Non-conjugated Dienes with $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ Catalyst System: Effect of Polymerization Temperature on the Copolymer Structure, *European Polymer Journal* 36 (2000) 183-192.

© 2000 Elsevier Science

Reprinted with permission from Elsevier.

Copolymerization of ethylene and non-conjugated dienes with $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst system: effect of polymerization temperature on the copolymer structure

Pirjo Pietikäinen^a, Jukka V. Seppälä^{a,*}, Lisbeth Ahjopalo^b, Lars-Olof Pietilä^b

^aDepartment of Chemical Engineering, Helsinki University of Technology, PO. Box 6100, Fin-02015 HUT, Espoo, Finland

^bVTT Chemical Technology, PO. Box 1401, FIN-02044 VTT, Finland

Received 8 May 1998; received in revised form 15 December 1998; accepted 15 January 1999

Abstract

Ethylene was copolymerized with linear, non-conjugated dienes by the metallocene catalyst system $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ at several temperatures from 20 to 80°C. The dienes were 1,5-hexadiene (HD), 1,7-octadiene (OD) and 7-methyl-1,6-octadiene (MOD). Incorporation of the dienes was studied by ^1H and ^{13}C NMR and FTIR. Polymerization conditions had a dramatic effect on the degree of crosslinking of the product. At polymerization temperatures from 20 to 65°C the copolymers of ethylene and HD or OD were nearly totally crosslinked, whereas at 80°C the degree of crosslinking was consistently under 10%. When MOD was used as comonomer the degree of crosslinking did not increase above 40% even for copolymer produced at 20°C. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Metallocene catalysts have proven to be effective in olefin as well as diene copolymerizations. Although the copolymerization of olefins with dienes has been studied with heterogeneous catalysts, little work has been reported on the copolymerization of olefins with non-conjugated dienes initiated by homogeneous metallocene catalysts.

The diversity of possible structures in ethylene/diene copolymers provides an interesting field for study. Unsaturated polyethylene would be a useful intermediate in the production of functionalized [1–3] or vulcanized polymers. In addition, ring structures might change the rheology of the polymer in a favorable manner in regard to processability. Rings can be cre-

ated in polyethylene chain by copolymerizing the ethylene with cycloalkenes [4–6], norbornenes [7,8] or linear dienes such as 1,3-butadiene [9,10] or 1,5-hexadiene (HD) [11–16]. Of particular interest is the capability of HD to produce five-member (cyclopentane) rings in the polyethylene chain. The crosslinking of the copolymer is still a severe problem in the case of α -olefin copolymerization with linear, non-conjugated dienes. The material is processable only if the degree of crosslinking is under 2%.

Polymerization temperature has a marked effect on the structure of the polymer and the effect varies with the reactivity and solubility of the monomer, the catalyst activity and the rate of mass transfer reactions. The present work was carried out to clarify the temperature dependencies of the reactions of ethylene and non-conjugated dienes: 1,5-hexadiene, 1,7-octadiene (OD) and 7-methyl-1,6-octadiene (MOD). Polymerizations were conducted at several tempera-

* Corresponding author. Fax: +358-9-4512622.

tures between 20 and 80°C in the presence of the metallocene catalytic system dicyclopentadienyl zirconium dichloride/methylaluminoxane (Cp₂ZrCl₂/MAO). Molecular modeling was carried out to study the probability of ring formation of the dienes. In this paper, we report on the degree of crosslinking, diene content, melt temperature and crystallinity and the structure of the copolymer as determined by NMR. Results are compared with those reported [17] earlier for a polymerization temperature of 90°C.

2. Experimental

2.1. Apparatus and polymerization method

Copolymerizations were performed in a 0.5-dm³ stainless steel reactor at ethylene pressure 2.5 bar at several temperatures between 20 and 80°C. A propeller-like stirrer was used at 550 rpm to stir the reaction mixture. The evacuated and N₂-purged reactor was filled with 0.25 dm³ *n*-heptane and heated to polymerization temperature. After this, diene was injected and cocatalyst (MAO) was pumped to the reactor. The Al/Zr mole ratio was 2000 in most of the polymerizations but 4000 where diene concentration was greater than 0.4 mol/dm³. No hydrogen was used. Feeding of ethylene was then begun and pressure was regulated to the desired level. Once equilibrium in ethylene dissolution was reached, the catalyst solution (5 mg/cm³ of Cp₂ZrCl₂ in toluene) corresponding to 1 mg of the catalyst was pumped to the reactor to start the polymerization. The ethylene pressure inside the reactor was maintained constant. Reactor temperature was controlled automatically with a Lauda R400 thermostat connected to a Pt-100 thermocouple. Accuracies of pressure and temperature control were ±0.1 bar and ±0.5°C, respectively. After 15 min polymerization, the ethylene feed was stopped and the reactor was degassed. The polymer solution was first washed with a solution of tech. methanol and conc. hydrochloric acid (1 : 0.1) overnight and then with methanol alone for an additional 3 h. The unreacted diene was washed out of the polymer in three consecutive extractions with pentane (100 ml/10 g sample). The polymer was dried in vacuum at 70°C for 1 hour.

2.2. Chemicals

Ethylene was grade 3.5 (from AGA). It was further purified just before feeding to the reactor by conduction through columns containing molecular sieves, Cu and Al₂O₃. Heptane was grade RG from JT Baker and toluene was grade RG from Riedel-de Hën. Liquid hydrocarbons were purified by making them flow

through three columns filled with molecular sieves (4 Å), Cu and Al₂O₃.

1,5-hexadiene (95%) and 1,7-octadiene (98%) were from Aldrich and 7-methyl-1,6-octadiene (97.3%) was from Shell. Dienes were purified with molecular sieves in their storage flasks.

The catalyst was soluble metallocene biscyclopentadienyl zirconium dichloride (Cp₂ZrCl₂) from Witco and the cocatalyst 10 wt% methylaluminoxane (MAO) in toluene from Schering.

2.3. Analysis

Melt temperatures of the product were determined by Polymer Laboratories DSC. The temperature range used was 0–165°C and melting as well as cooling were carried out at 10°C/min. The results from the second melting were recorded. The crystallinities were determined by using value 290 J/g for the heat of fusion of a 100% crystalline polyethylene.

NMR measurements were carried out with a Varian GEMINI 2000 NMR spectrometer to determine the amount of diene in the copolymer product. The sample was dissolved in deuterated tetrachloroethane. Measurements were carried out at 125°C.

A Nicolet FTIR (Magna-IR 750) was used for the determination of unsaturations in the copolymers. Measurements were carried out on 0.5 mm thick sample plates compressed at 200°C. Double bond concentrations per 1000 carbon atoms were calculated according to Haslam et al. [18]

The degree of crosslinking was determined by decaline extraction based on ASTM standard D-2765-84 [19]. Samples were weighed into bags of brass net (100 mesh) and extracted in a Soxhlet apparatus for 6 h and dried in vacuum at 150°C for 30 min.

A Waters 150-C ALC GPC instrument was used to determine the molar mass and the molar mass distribution of the samples. The instrument was equipped with PL-gel columns of particle sizes 10⁻³, 10⁻⁵ and 10⁻⁶ Å. The solvent was 1,2,4-trichlorobenzene, fed at a flow rate of 1.0 cm³/min at 140°C. Narrow molar mass polystyrene standards were used for calibration.

The conformational analyses in this work were performed with high-temperature molecular dynamics (MD) using the *Discover* 95.0/3.0.0 program by MSI [20]. The pcff field was used in all the molecular mechanics (MM) and dynamics calculations. The graphical displays were printed out from the *Insight* II molecular modeling system [21]. All the quantum chemical calculations were carried out with the DMol version 95.0 [22] using the B-LYP functional [23,24] and DND basis set.

Table 1

Polymerizations of ethylene and 1,5-hexadiene (HD) with the catalyst system $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ and the characterization of the product. Polymerizations were conducted in 250 cm^3 heptane; ethylene pressure 2.5 bar; amount of catalyst 1 mg; Al/Zr molar ratio 2000 (4000 for $[\text{HD}] > 0.4$); polymerization time 15 min

Run	T_{pol} (°C)	HD (mol/dm ³)	Activity (kg pol/(mol Zr h))	T_{m} (°C)	Crystallinity (%)	Link (%)	\bar{M}_w^a (g/mol)	\bar{M}_w/\bar{M}_n
1	20	0.02	1.0	133	38	> 80	357,000	2.5
2	20	0.06	3.6	128	32	> 80	nd	nd
3	50	0	2.6	137	35	< 0.2	356,000	2.2
4	50	0.005	2.6	130	27	29	432,000	2.4
5	50	0.02	4.3	129	32	45	421,000	2.8
6	50	0.06	4.2	129	35	> 80	315,000	3.4
7	50	0.36	7.1	107	26	< 80	nd	nd
8	65	0	4.8	137	47	72	nd	nd
9	65	0.02	5.0	132	39	51	nd	nd
10	65	0.06	5.6	126	29	65	nd	nd
11	80	0	7.8	135	55	< 0.2	70,000	2.5
12	80	0.002	7.8	141	60	0.8	71,000	2.6
13	80	0.02	10.0	134	46	1	100,000	2.7
14	80	0.06	7.0	130	47	0.8	60,000	3.0
15	80	0.36	6.7	110	40	0.9	27,000	5.8
16	80	0.73	6.2	99	27	< 0.2	27,000	3.0

^a Measured of the soluble part of the sample.

3. Results and discussion

Polymerizations and product characterizations are presented in Tables 1–3. The characterization includes the results of DSC (melt temperature, T_{m} and crystallinity, Cryst) and GPC measurements (weight average molar mass, M_w and polydispersity, M_w/M_n) and the degree of crosslinking (Link).

As can be seen in Table 1, at temperatures lower than 80°C the activity of the catalyst tended to increase with addition of HD to the reaction mixture. A similar rate enhancement effect has been reported to occur with 1,4-hexadiene as comonomer [25] and in ethylene/ α -olefin copolymerizations [26–32]. At 80°C the reactivity seemed to be relatively independent of the HD concentration in the reactor. In the cases of

Table 2

Polymerizations of ethylene and 1,7-octadiene (OD) with the catalyst system $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ and the characterization of the product. Polymerizations were conducted in 250 cm^3 heptane; ethylene pressure 2.5 bar; amount of catalyst 1 mg; Al/Zr molar ratio 2000 (4000 for $[\text{MOD}] > 0.4$); polymerization time 15 min

Run	T_{pol} (°C)	OD (mol/dm ³)	Activity (kg pol/(mol Zr h))	T_{m} (°C)	Crystallinity (%)	Link (%)	\bar{M}_w^a (g/mol)	\bar{M}_w/\bar{M}_n
17	20	0.01	0.9	131	37	> 80	nd	nd
18	20	0.04	1.9	127	21	> 80	nd	nd
19	20	0.003	3.2	131	31	> 80	nd	nd
20	50	0.01	3.9	124	24	> 80	nd	nd
21	50	0.03	2.4	125	29	> 80	nd	nd
22	50	0.04	4.0	122	20	> 80	nd	nd
23	65	0.01	4.5	126	30	> 80	nd	nd
24	65	0.04	4.4	120	17	> 80	nd	nd
25	65	0.14	3.0	114	16	> 80	nd	nd
26	80	0.01	3.3	129	44	9.3	19,000	4.8
27	80	0.04	6.4	118	40	10	32,000	4.0
28	80	0.08	4.0	113	33	10	33,000	3.1
29	80	0.27	4.5	102	18	0.4	17,000	6.3
30	80	0.68	4.4	nd	nd	29	3500	2.2

^a Measured of the soluble part of the sample.

Table 3

Polymerizations of ethylene and 7-methyl-1,6-octadiene (MOD) with the catalyst system $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ and the characterization of the product. Polymerizations were conducted in 250 cm³ heptane; ethylene pressure 2.5 bar; amount of catalyst 1 mg; Al/Zr molar ratio 2000 (4000 for [MOD] > 0.4); polymerization time 15 min

Run	T_{pol} (°C)	MOD (mol/dm ³)	Activity (kg pol (mol Zr h))	T_{m} (°C)	Crystallinity (%)	Link (%)	\bar{M}_w^a (g/mol)	\bar{M}_w/\bar{M}_n
31	20	0.12	0.6	122	42	41	20,000	2.2
32	20	0.48	1.4	104	21	9	49,000	3.3
33	50	0.04	1.9	128	35	0.9	115,000	2.5
34	50	0.12	5.0	115	35	4	51,000	2.1
35	50	0.24	3.3	114	25	5	40,000	2.2
36	50	0.48	2.7	105	22	4	15,000	1.9
37	80	0.04	4.0	124	40	8	36,000	2.1
38	80	0.12	3.5	116	37	8	8000	3.0
39	80	0.24	1.6	107	40	10	4300	2.1
40	80	0.48	2.9	93	17	6	7400	2.2

^a Measured of the soluble part of the sample.

OD and MOD (Tables 2 and 3), there was no clear response of catalyst activity to the diene concentration in the reactor.

3.1. Diene incorporation

Diene incorporation into polyethylene chain was studied by NMR techniques only for limited amounts of sample because crosslinked copolymers are poorly soluble. Additional information was obtained by FTIR analysis. For crosslinked samples the decrease of melt temperature and crystallinity of the product can be taken as an indication of incorporation of dienes.

¹³C-NMR analysis showed that at 80°C HD was incorporated into the polyethylene chain exclusively in the form of cyclopentane structures attached at their 1 and 3 positions to the polymer backbone and about 24% of the rings were in *cis* conformer. The same was the case for copolymers obtained at 90°C [17]. HD-containing samples prepared at temperatures lower than 80°C did not dissolve in deuterated tetrachloroethane and could not be analyzed by NMR. However, films for FTIR analysis could be compressed from some of the crosslinked samples and the existence of five-member rings could be seen in the spectra at wavenumbers 875 and 945 cm⁻¹, which are due to the oscillations of CH₂ groups of the ring. As expected, FTIR revealed a tendency towards decreasing amount of double bonds with decreasing polymerization temperatures when the product was strongly crosslinked.

Comparison of ethylene/HD and ethylene/1-butene [22] copolymers is of interest since both copolymers contain a propyl branch, though in the case of HD copolymer it is fixed at both ends to the polyethylene chain. Although the values reported for ethylene/1-

butene refer to polymerizations conducted under experimental conditions that were neither identical with ours nor optimized, it can be seen that branches disturb the structure more than rings and the melt temperature and molar mass of ethylene/1-butene copolymers were lower than those of ethylene copolymers with HD.

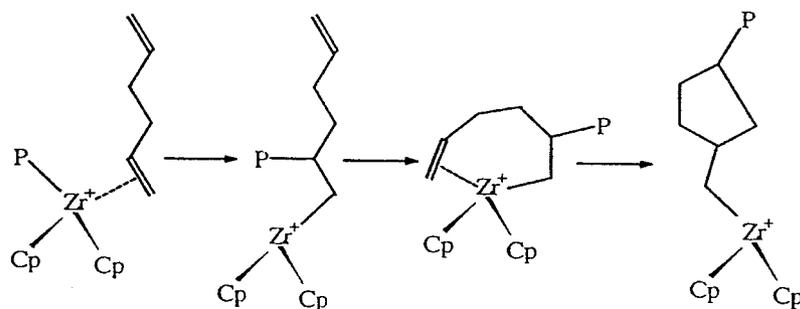
OD is incorporated into the polyethylene as hexene branches either as single branches or branch pairs, as has been reported earlier in Ref. [17]. In theory it would be possible for OD to form rings to polyethylene chain, but this did not occur under our experimental conditions. The ratio of single branches to branch pairs increased from 0.25 to 1.25 when the OD concentration in the reactor was increased from 0.08 to 0.27 mol/dm³.

Only the OD samples produced at 80°C could be analyzed by NMR, owing to poor solubility of the copolymer. FTIR analysis was carried out on samples for which film could be obtained and the results showed a significant drop in the amount of free double bonds as the temperature of polymerization decreased. This is again in good accordance with the high degree of crosslinking in these samples.

MOD forms 6-methyl-hexene branches in the polyethylene chain as expected [17]. The branch structure was the same at all temperatures at which determination was possible. FTIR did not provide any additional information for the MOD-containing copolymers because the absorbance of the end group of the 6-methyl-hexene branch is overlapped by the peak of the CH₂ oscillation of the polyethylene chain at 720 cm⁻¹.

In order to clarify the formation of rings in ethylene/diene copolymers, we studied the structures of HD, OD and MOD in combination with Cp_2ZrCl_2

catalyst by molecular modeling. Cavallo et al. [13] proposed the mechanism



for the ring formation reaction for HD. According to this mechanism, the carbon atoms 2 and 6 in 1-hexene have to come into proximity in order to make the ring closure possible. In B-LYP/DND optimized structure of the π -complex $\text{Cp}_2\text{ZrCH}_3(\text{CH}_2=\text{CH}_2)^+$ of the model system for the olefin insertion reaction of metallocene catalyzed polymerization, the $\text{C}\cdots\text{C}$ distance of the forming bond was 3.25 Å.

Two hundred and fifty structures of 1-hexene were generated using high temperature molecular dynamics and subsequent energy minimization. In the energy minimization the structures converged into a few distinct conformers. The conformational energy is displayed as a function of the $\text{C}_2\cdots\text{C}_6$ distance in Fig. 1. Energies of all conformers were 3.5 kcal/mol or less above the global minimum and, thus, the conformers are easily accessible, especially at elevated temperatures. For one conformer, which is shown in Fig. 1, the $\text{C}_2\cdots\text{C}_6$ distance was 3.29 Å, i.e. close to the optimum value, while the energy was 2.2 kcal/mol. When this conformer was superimposed on the π -complex

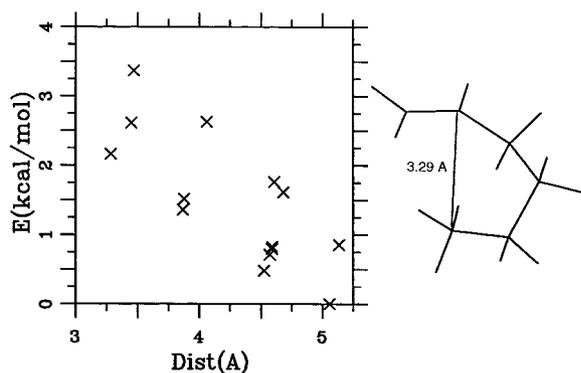


Fig. 1. Conformational analysis of 1-hexene. The distance is the $\text{C}_2\cdots\text{C}_6$ distance relevant for ring formation and the structure is that with the shortest $\text{C}_2\cdots\text{C}_6$ distance.

(the double bond of the 1-hexene in the ethylene molecule in the π -complex), there was only a little hindrance. The shortest $\text{H}\cdots\text{H}$ and $\text{H}\cdots\text{C}$ distances are 2.03 and 2.5 Å, respectively. The superimposed structures are displayed in Fig. 2. The surfaces shown are van der Waals surfaces of the relevant atoms. Because of the flexibility of the π -complex of the catalyst, these repulsions are easily reduced by minor adjustments of the geometry of the π -complex.

Since the chains are longer, there are many more conformers of OD and MOD than of HD. Fig. 3 and Fig. 4 shows the $\text{C}\cdots\text{C}$ distance–energy graphs for 1-octene and 1-methyl-2-octene, calculated in a similar way as in Fig. 1 for 1-hexene. In 1-octene, the conformers having the relevant $\text{C}_2\cdots\text{C}_8$ distance of about

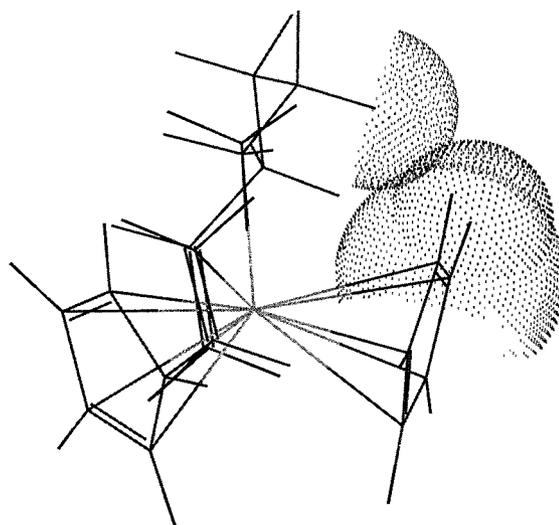


Fig. 2. The conformer of 1-hexene with the shortest $\text{C}_2\cdots\text{C}_6$ distance superimposed on the B-LYP/DND optimized structure of the π -complex $\text{Cp}_2\text{ZrCH}_3(\text{CH}_2=\text{CH}_2)^+$. The double bond of 1-hexene is superimposed on the ethylene molecule in the π -complex.

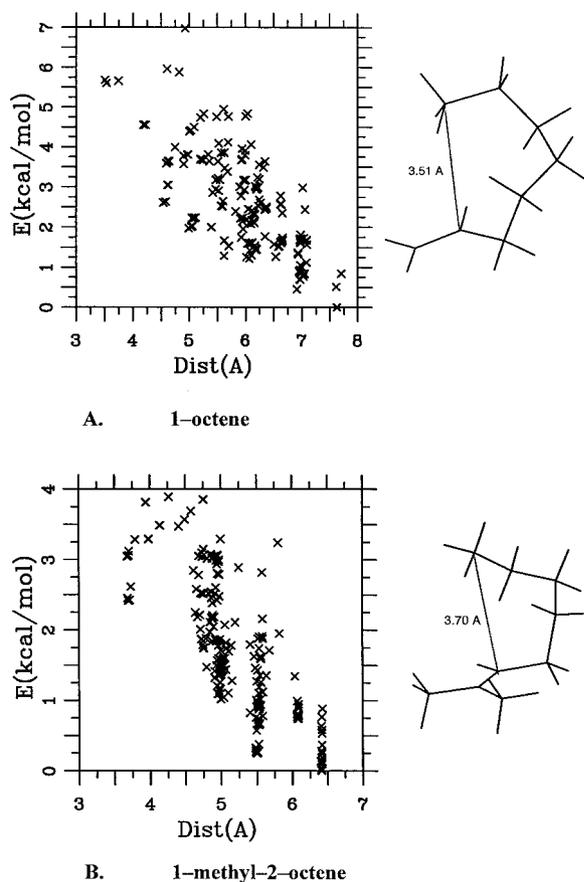


Fig. 3. Conformational analysis of 1-octene (A) and 1-methyl-2-octene (B). The C...C distances are the ones which are relevant for the possible ring formation reaction; A: C₂...C₈ and B: C₃...C₈. The structures are examples of those with short relevant C...C distances.

3.5 Å have energies about 5.5 kcal/mol higher than the global minimum, which gives them a relatively low population. When these conformers are superimposed on the π -complex of the catalyst, there is some steric hindrance. The shortest H...H and H...C distances, (1.2–1.6 Å and 1.9–2.3 Å) are much shorter than the sum of the van der Waals radii of the atoms (hydrogen 1.22 Å and carbon 1.7 Å). Owing to the flexibility of the π -complex, the system can relax to relieve the strain, but at the cost of increasing the energy in other terms. The low population and the steric hindrance make the ring formation reaction of the OD comonomer highly improbable. In 1-methyl-2-octene, there are a few conformers in which the relevant C₃...C₈ distance is about 3.7 Å and these have energies 2–3 kcal/mol higher than the global minimum. The ring formation reaction is ruled out by severe steric hindrance, however, as was seen by superimposing these conformers on the π -complex of the catalyst.

The amounts of OD and MOD in the product (Fig. 4) could be calculated on the basis of unsaturations in the product determined by ¹H NMR, since every incorporated octadiene unit brings a double bond to the polyethylene chain. The HD is exclusively incorporated as five-member (cyclopentane) rings, as noted in our earlier study [17] and the amount of HD was determined therefore from ¹³C-NMR measurements. The amounts of diene in the product were large enough that the double bonds caused by the chain end reactions in ethylene homopolymerization could be neglected. At 80°C, OD and MOD were better incorporated into polyethylene chain than was HD. Copolymers containing up to 7.7 mol% HD and 9.0 mol% OD were obtained at 80°C.

For copolymers obtained at 80°C, the conversion of HD clearly decreased (from 50 to 2%) when diene concentration in the reactor was increased and the same was true to a lesser extent for conversion of MOD (from 9 to 2%). At polymerization temperature of 50°C, however, the conversion of MOD was nearly constant (at 2%). In ethylene/OD copolymerizations at 80°C the conversion varied from 6 to 13%. The conversion of diene monomers decreased sharply when the temperature was decreased from 90 to 80°C [17]. Evidently, ethylene concentration plays an important role in diene incorporation. At lower temperatures the reactivity of ethylene decreases more strongly than the reactivity of dienes and ethylene is thus less likely to react with another ethylene molecule than with diene.

3.2. Determination of copolymerization parameters

In general, reactivity ratios are calculated from the ¹³C-NMR spectra according to the method of Kaguro et al. [33]. In the case of our ethylene/diene copolymers, however, the required triad sequence distributions could not be calculated from the NMR results and instead, we used the Fineman–Ross equation [34] to determine the reactivity ratios (see Table 4). The reactivity ratios r_E/r_D were nearly one and independent of the structure of the diene comonomer, which confirmed the formation of random copolymers in all our experiments.

3.3. Crosslinking

As can be seen in Tables 1 and 2, polymerization temperature had a dramatic effect on the degree of crosslinking in the HD- and OD-containing products. For products containing HD or OD, even very small amounts of diene in the reactor produced high degrees of crosslinking at polymerization temperatures of 20 and 50°C (Tables 1 and 2). This is again due to the varying reactivity of the monomers with temperature. Relative to that of dienes, the reactivity of ethylene is

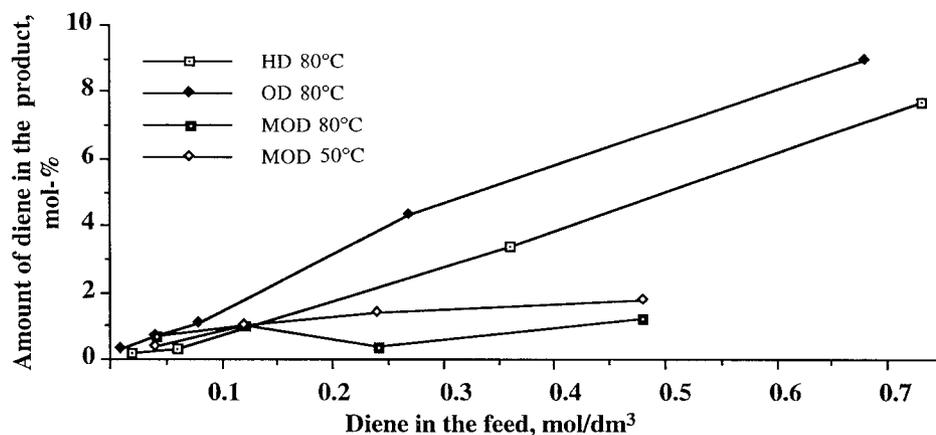


Fig. 4. The amount of diene in the ethylene copolymers as a function of diene concentration in the reactor. Polymerizations were conducted with $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst system in 250 cm^3 heptane; ethylene pressure 2.5 bar; amount of catalyst 1 mg; Al/Zr molar ratio 2000 (4000 for $[\text{MOD}] > 0.4$); polymerization time 15 min. HD = 1,5-hexadiene, OD = 1,7-octadiene, MOD = 7-methyl-1,6-octadiene.

so low at these temperatures that the amount of diene in the product is high enough to produce considerable crosslinking. It also seemed that higher polymerization temperatures favoured ring formation in HD-containing copolymers. This might be understood as follows: a prerequisite for ring formation is that the free end of the butene branch that is first formed in the polyethylene chain comes into proximity with the growing chain and the probability of this happening is increased at higher temperature.

For copolymers of OD polymerized at 50°C the crosslinking was nearly 100% for lowest diene contents but decreased significantly between diene concentrations of 0.04 and 0.27 mol/dm^3 . On the other hand, in the copolymers containing HD, at the same polymerization temperature (50°C), crosslinking remained at 100% for all levels of HD addition. Results for the OD-containing copolymers produced at 65°C were about the same as for those produced at 50°C : the degree of crosslinking decreased from 90% to about

15% between OD concentrations of 0.01 and 0.14 mol/dm^3 . At 80°C , the degree of crosslinking was consistently under 10% for both HD and OD copolymers and at 90°C it was less than 2% for all HD and OD concentrations [17]. Increasing polymerization temperature increases the reactivity of ethylene much more than the reactivity of dienes, so that the probability of the diene being polymerized from both ends, i.e. to be crosslinked, decreases, even though the amount of diene in the product increases.

When MOD was used as comonomer the degree of crosslinking did not increase above 40% even for copolymer produced at 20°C (Table 3). This was as expected, since the methyl group in MOD protects the second double bond, which remains unreacted in the polymerization. For all diene additions, the degree of crosslinking in ethylene/MOD copolymers produced at 50°C was less than 10% and at 80°C it was almost 0%.

3.4. Molar mass

The effect of polymerization temperature on the molar mass could only be measured for MOD copolymers, since the other diene comonomers were crosslinked at temperatures lower than 80°C . Note, too, that the molar masses reported should be considered as indicative values since even at 80°C there could be some minor crosslinking. In general, increasing polymerization temperature decreases the molar mass of a polymer. This can clearly be seen for our homopolymer but even a small addition of MOD reduced the molar mass to such a low level that no significant trends in the polymerization temperatures could be observed. The molar masses of all the MOD-contain-

Table 4

The reactivity ratios for ethylene/diene copolymerization determined using the Fineman–Ross equation (HD = 1,5-hexadiene, OD = 1,7-octadiene, MOD = 7-methyl-1,6-octadiene)

Diene	r_E	r_D	r_E/r_D
HD ^a	1.03	0.91	0.94
OD ^a	1.04	0.91	0.95
MOD ^b	1.02	0.98	1.00
MOD ^a	1.01	1.00	1.01

^a Polymerization temperature 80°C .

^b Polymerization temperature 50°C .

ing copolymers obtained at 80°C were below 10,000 g/mol.

Increasing the comonomer concentration in the reaction medium decreased the molar mass of the copolymers, which underlines the role of comonomer in the reduction of the ratio of chain propagation to chain termination rate. Reasons for the reduction may be the lower rate of comonomer insertion, enhanced chain transfer to comonomer and more facile β -H elimination from the comonomer due to the tertiary nature of its β -hydrogen atom [35].

Comparison of the effect of the different dienes on the molar mass of the copolymer showed that HD did not decrease the molar mass as much as OD and MOD did, particularly at high diene concentrations. This is in agreement with the general observation that shorter olefins decrease the molar mass less. Furthermore, the ring formation reaction in the case of HD, where the insertion of the first double bond is followed by the incorporation of a second for the same monomer, decreased the chain propagation reaction rate less than did the 1,2-insertion of either OD or MOD.

In the case of ethylene/OD copolymers, polydispersity increased dramatically when the diene content in the product was increased at 80°C. The polydispersities varied from 2.5 (homopolyethylene) to 7 (9.0 mol% OD in copolymer). At the same time, weight average molar mass decreased from 117,000 g/mol to 3500 g/mol. Molar mass distributions of ethylene/HD copolymer samples ranged from 2.5 to 2.9 and those of ethylene/MOD from 2 to 3.5. In both cases the distribution broadened with increasing polymerization temperature and diene content of the copolymer.

The broadening of the molar mass distribution in the case of OD is due to the relatively large diene contents in copolymers with very low molar masses. MOD copolymers also had low molar masses, but the amount of diene incorporated was less (Fig. 4) and therefore the effect on molar mass distribution was less pronounced. The addition of HD comonomer did not decrease the molar mass as much as octadienes did and hence it had only minor effect on the molar mass distribution.

3.5. Melt temperature and crystallinity

The thermal behavior of the ethylene/diene copolymers was dependent on the polymerization temperature and the level of incorporated diene. In our experiments, the melt temperature was depressed with increasing diene concentration in the reactor, as was expected, since both melt temperature and crystallinity of the copolymer decrease with the density of side chain. This can be taken as a strong indication of the increasing amount of diene in the copolymer, even

though the amount of diene cannot be determined in products obtained at temperatures lower than 80°C. Tables 1–3 show the effect of feed as well as of polymerization temperature on the melt temperature of the product. As some melting always takes place at the uncrosslinked chain ends, melt temperature was also detected for the crosslinked samples.

The structures of the dienes had their characteristic effects on the melt temperature and crystallinity of the copolymer. When OD or MOD was the comonomer the melt temperature decreased as the polymerization temperature increased from 20 to 80°C, but no such effect was found for HD. Clearly, the unsaturated side chains of OD and MOD copolymers disturb the crystallization process of polyethylene chain more than the ring structures formed by HD and the melt transitions of OD and MOD copolymers noticeably decreased relative to those of the ethylene homopolymer synthesised under the same conditions. This can be seen (Tables 1–3) when the same amount of diene is incorporated.

The melt temperature decreases with increasing polymerization temperature because the molar mass of the product decreases and the diene incorporation in most cases becomes more effective. The more effective incorporation can be seen in the broader melt behavior at lower melt temperatures, indicating microstructural heterogeneity. The heterogeneity might be the result of changes in the diene concentration relative to ethylene during the copolymerization, giving a non-uniform distribution of incorporated diene units over the polymer chains.

The crystallinity results were in accord with the melt temperature results. Given to the strong effect of reaction temperature on the melt temperature, it was no surprise that the crystallinity of the copolymer was most affected by OD and least by HD addition.

4. Conclusions

In conclusion, with the metallocene catalyst system $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$, dienes can be copolymerized with ethylene in reasonable conversions and a large variety of products can be produced by varying the temperature of polymerization and the type and amount of diene. Molecular modeling confirmed what was shown earlier experimentally [15–17,29], that there is hardly any steric hindrance in the ring formation for the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyzed copolymerization of ethylene and HD. Ring formation is not completely ruled out in the ethylene/OD copolymerization, but it is improbable, partly for steric reasons and partly because of low population of the conformers of OD monomer suitable for the ring closure reaction. In eth-

ylene/MOD copolymerization, ring formation is ruled out by strong steric hindrance.

NMR studies showed that, at 80°C, HD was exclusively incorporated as five-member rings, while OD formed either single branches or branch pairs. The branches obtained upon copolymerization with MOD were 6-methyl-hexene branches, which was the expected form of incorporation for this comonomer. At lower temperatures the samples were studied by FTIR and the concentration of double bonds was significantly higher in OD-containing copolymers than in the other copolymers studied. The large amount of vinyl bonds in the OD copolymers made functionalization possible.

The marked influence of catalyst structure and polymerization conditions in HD copolymerizations becomes evident in a comparison of our results with those of other groups. With Cp_2ZrCl_2 as catalyst, neither diene concentration nor polymerization temperature affected the copolymer structure: the diene was incorporated exclusively as cyclopentane rings and the ratio between *cis* and *trans* configuration remains constant. However, with $\text{Me}_2\text{Si}(\text{THInd})_2\text{ZrCl}_2$ [15,16] as well as with $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(N\text{-tert-butyl})\text{TiCl}_2$ [36] as catalysts in terpolymerization where styrene is the other comonomer, both rings and branches with vinylic unsaturation have been obtained at high temperature (180°C) and pressure (1500 bar).

The polymerization temperature has a significant effect on the degree of crosslinking of the product when symmetric dienes provide the comonomer. While the degree of crosslinking was nearly 100% in all copolymers produced at 20°C, in all HD copolymers produced at 50°C and in OD copolymers prepared from small amounts of diene at 50°C, it was less than 10% in products prepared at 80°C. At this higher temperature, however, the molar mass of the product was low, the weight average molar mass being maximally 100,000 g/mol and dropping off sharply with increasing amount of added diene. The molar mass also decreased with increasing diene content in the product. The methylene group in MOD protects the unreacted double bond and the degree of crosslinking was negligible in copolymers containing this diene. From the point of view of crosslinking, MOD would thus be an excellent comonomer in ethylene copolymerizations. However, it decreases the molar mass of the copolymer significantly and is not efficiently enough incorporated in the polyethylene chain. The methylene substitution at the unsaturated branch end also reduces its value if the product is to be used as intermediate in functionalization of the copolymer.

Increased amount of diene in the product decreased both melting temperature and crystallinity. OD seemed to have the greatest influence on both of these properties, as well as on the molar mass of the product. The

analysis of unsaturations revealed up to 28 wt% incorporation of OD in the product. Our studies on these copolymers by thermal methods and DMTA have been reported elsewhere [37].

References

- [1] Marathe S, Sivram S. *Macromolecules* 1994;27:1083.
- [2] Chung TC, Lu HL, Li CL. *Macromolecules* 1994;27:7533.
- [3] Lee D-H, Yoon K-Y, Park J-R, Lee B-H. *Eur Polym J* 1997;33:447.
- [4] Kaminsky W, Spiehl R. *Makromol Chem* 1989;190:515.
- [5] Welborn HC. *Unsaturated ethylene polymers*, WO 8804674, 1988.
- [6] Kaminsky W, Bark A, Arndt M. *Makromol Chem, Macromol Symp* 1991;47:83.
- [7] Kaminsky W, Miri M. *J Polym Sci, Polym Chem Ed* 1985;23:2151.
- [8] Chien CW, He D. *J Polym Sci, Part A* 1991;29:1609.
- [9] Welborn HC. *Copolymers of ethylene and 1,3-butadiene*. WO 8804672, 1988.
- [10] Galimberti M, Albizzati E, Abis L, Bacchilega G. *Makromol Chem* 1991;192:2591.
- [11] Austin RG, Welborn HC, Jr. *Ethylene copolymers*. WO 88/04673, 1988.
- [12] Resconi L, Coates GW, Mogstad A, Waymouth RM. *J Macromol Sci -Chem* 1991;A28:1225.
- [13] Cavallo L, Guerra G, Corradini P, Resconi L, Waymouth R. *Macromolecules* 1993;26:260.
- [14] Coates GW, Waymouth RM. *J Am Chem Soc* 1993;115:91.
- [15] Bergemann C, Cropp R, Luft G. *Chemie Ingenieur Technik* 1996;68:417.
- [16] Bergemann C, Cropp R, Luft G. *J Molek Catal A Chemical* 1997;116:317.
- [17] Pietikäinen P, Väänänen T, Seppälä J. *Eur Polym J* 1999;35:1047.
- [18] Haslam J, Willis HA, Squirrell DCM. In: *Identification and analysis of plastics*, 2nd ed. London: Butterworth, 1972. p. 372.
- [19] ASTM D-2765-84. *Standard test methods for determination of gel content and swell ratio of crosslinked ethylene plastics*.
- [20] *Discover 95.0/3.0.0 User Guide*. October 1995, San Diego: Biosym/MSI, 1995.
- [21] *Insight II User Guide*. October 1995, San Diego: Biosym/MSI, 1995.
- [22] *DMol Version 95.0*, October 1995, San Diego: Biosym/MSI, 1995.
- [23] Becke AD. *J Chem Phys* 1988;88:2574.
- [24] Lee C, Yang W, Parr RG. *Phys Rev B* 1988;37:785.
- [25] Chung TC, Lu HL, Li CL. *Macromolecules* 1994;27:7533.
- [26] Koivumäki J, Seppälä J. *Macromolecules* 1993;26:5535.
- [27] Seppälä JV, Koivumäki J, Liu X. *J Polym Sci, Part A: Polym Chem* 1993;31:3447.
- [28] Koivumäki J, Seppälä JV. *Macromolecules* 1994;27:2008.
- [29] Tsutsui T, Kashiwa N. *Polym Commun* 1988;29:180.

- [30] Chien JCW, Nozaki T. *J Polym Sci Part A* 31 1993;31:227.
- [31] Herfert P, Montag P, Fink G. *Macromol Chem* 1993;194:3167.
- [32] Tsui WM, Chien JCW. *J Polym Sci Part A* 1994;32: 149.
- [33] Kakugo M, Naito K, Mizunuma IC, Miyazake T. *Macromolecules* 1992;15:1150.
- [34] Fineman M, Ross S. *J Polym Sci* 1950;5:259.
- [35] Lehmus P, Härkki O, Leino R, Luttikhedde HJG, Näsman JH, Seppälä JV. *Macromol Chem Phys* 1997;199:1965.
- [36] Sernez FG, Mülhaupt R, Waymouth RM. *Polym Bull* 1997;38:141.
- [37] Pietikäinen P, Starck P, Seppälä J. *J Polym Sci Part A: Polym Chem*, in press.