PERGAMON

European Polymer Journal 35 (1999) 1047–1055

EUROPEAN POLYMER JOURNAL

Copolymerization of ethylene and non-conjugated dienes with Cp_2ZrCl_2/MAO catalyst system

P. Pietikäinen[a, *], T. Väänänen[b], J.V. Seppälä[a]

[a]Department of Chemical Technology, Helsinki University of Technology, P.O.B. 6100, SF-02015 HUT, Finland
[b]Neste Oy, Technology Center, P.O.B. 310, 06101 Porvoo, Finland

Received 9 March 1998; accepted 6 July 1998

Abstract

Ethylene was copolymerized with linear, non-conjugated dienes by the metallocene catalyst system Cp_2ZrCl_2/MAO at 90°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. According to the results, HD formed only five-member rings to polyethylene, even though selectivity towards cyclization has been reported to decrease when HD concentration in the reactor increases over 50 mol%. OD and MOD were incorporated by 1,2-addition forming branches to the copolymer. The conversion of MOD remained under 4%, and was noticeably lower than that of HD and OD (25–40%). However, the effect of MOD on the physical properties of the copolymer was significant, whereas HD addition had almost no effect on the molar mass. The conversion of all dienes decreased when the diene concentration in the reactor was increased. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Metallocene catalysts have proven to be effective in olefin/diene copolymerizations. In general, the homogeneous catalysts are much more effective than their heterogeneous counterparts in the incorporation of diene comonomers in polyethylene structure. Both linear and cyclic dienes have been incorporated [1–13]. The copolymerization of dienes with ethylene may introduce unsaturation in polymer chains making possible the attachment of functional groups. Recently, a few successful examples have been reported of polyethylenes unsaturated by dienes that have acted as intermediates for functionalized polyolefins [14–16]. These functionalized polyolefins can serve as interfacial modifiers to improve the adhesion and compatibility of polyolefins with other materials.

Besides unsaturation, copolymerization of dienes allows the construction of cyclic structures and long chain branching in the polyethylene backbone. A number of non-conjugated dienes, such as 1,5-hexadiene, 1,4-pentadiene and 1,7-octadiene, are capable of undergoing cyclopolymerization in the presence of coordination catalyst. Several reports have been published on 1,5-hexadiene (HD) homopolymerizations [17–24] but few on ethylene/HD copolymerizations using metallocene catalysts [25–27]. The homopolymer of HD is an optically active polyolefin consisting of consecutive five member rings. In ethylene/HD copolymers, HD is predominantly incorporated as rings in the polyethylene backbone but may also form long chain branching and intermolecular coupling [10]. On the other hand, modification reactions of polyolefins are usually accompanied by undesirable side reactions, such as the formation of gel in the polymer through incorporation of a second double bond as a crosslink in the copolymerization. A second complication is degradation.

We studied the effect of diene addition on the structure of ethylene copolymer at a polymerization temperature of 90°C. The dienes used were 1,5-hexadiene (HD), 1,7-octadiene (OD), and 7-methyl-1,6-octadiene (MOD). Polymerizations were conducted in n-heptane in the presence of the metallocene catalyst cyclopenta-

---

* Corresponding author. Fax: +358 9 451 26 22.

PII: S0014-3057(98)00192-X

dienyl zirconium dichloride (Cp_2ZrCl_2) with methylaluminoxane (MAO) as a cocatalyst. This basic metallocene was chosen in order to minimize the electronic and ligand effects in the polymerization.

2. Experimental

2.1. Apparatus and polymerization method

Copolymerizations were performed in a 0.5 dm^3 stainless steel reactor at ethylene pressure 2.5 bar at 90°C. A propeller-like stirrer was used at 550 rpm to stir the reaction mixture. The evacuated and N_2-purged reactor was filled with 0.25 dm^3 *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/dm^3. 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/dm^3 of Cp_2ZrCl_2 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 ±0.3 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 technical methanol and concentrated 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 h.

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 Al_2O_3. Heptane was grade RG from JT Baker and toluene was grade RG from Riedel-de Häen. Liquid hydrocarbons were purified by making them flow through three columns filled with molecular sieves (4 Å), Cu and Al_2O_3.

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 (Cp_2ZrCl_2) from Witco and the cocatalyst 10 wt% methylaluminoxane (MAO) in toluene from Schering. The Al content of the cocatalyst was 4.5–5.5 wt%.

2.3. Analysis

Melt temperatures of the product were determined by Polymer Laboratories DSC. The temperature range applied 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 the value 290 J/g for the heat of fusion of a 100% crystalline polyethylene.

NMR measurements were carried out with a Varian Gemini 2000 nuclear magnetic resonance spectrometer to determine the amount of diene in the copolymer product. The sample was dissolved in deuterated tetrachlorethane and measurements were carried out at 125°C.

A Nicolet FTIR (Magna-IR 750)instrument was used for the determination of unsaturations in the copolymers. Measurements were carried out from 0.5 mm thick sample plates compressed at 200°C. Double bond concentrations per 1000 carbon atoms were calculated according to Haslam and coworkers [28].

The degree of crosslinking was determined by decaline extraction based on ASTM standard D-2765-84 [29]. 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 used at a flow rate of 1.0 cm^3/min at 140°C. Narrow molar mass polystyrene standards were used for calibration.

3. Results and discussion

Ethylene/diene copolymerizations were carried out with a Cp_2ZrCl_2/MAO catalyst system in *n*-heptane at 90°C, with a polymerization time of 15 min and ethylene pressure of 2.5 bar. Polymerizations are summarized in Table 1.

3.1. NMR study of copolymer structure

As has been reported earlier [25–27], HD can be incorporated into the polyethylene chain as butene branches or in the form of cyclopentane structures connected at their 1 and 3 positions to the polymer

Table 1
Polymerizations of ethylene and dienes [1,5-hexadiene (HD), 1,7-octadiene (OD), 7-methyl-1,6-octadiene (MOD)] with the catalyst system Cp_2ZrCl_2/MAO at 90°C[a]

Run	Diene in the reactor, mol/dm^3	Activity of the catalyst, kg pol/mol Zr h	Melt temperature, °C	Crystallinity, %	Degree of crosslinking, %	$\bar{M}w$, g/mol	$\bar{M}w/\bar{M}n$
1	—	6.0	134	63	< 0.2	23,000	2.5
HD							
2	0.02	5.5	127	49	< 0.2	26,000	2.7
3	0.06	3.2	122	38	0.2	25,000	2.8
4	0.36	8.2	107	21	< 0.2	24,000	2.4
OD							
5	0.01	3.4	124	39	0.2	17,000	2.8
6	0.04	6.7	118	31	0.7	15,000	3.1
7	0.27	1.6	87	5	< 0.2	25,000	6.7
MOD							
8	0.04	7.5	123	39	0.2	13,000	2.2
9	0.12	4.8	113	35	0.7	8100	3.7
10	0.48	3.1	90	11	< 0.2	7700	3.6

[a] 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 [HD] > 0.4); polymerization time 15 min.

backbone. According to the ^{13}C–NMR spectra of sample 3 (Fig. 1), the copolymer contains no branching, only ring structures. No branching was found in any of our HD samples even though the selectivity for cyclization has been reported to decrease when the HD concentration in the reactor increases [25, 30].

HD was incorporated in the copolymers with conversion of 20–40% depending on the diene concentration in the reactor. According to ^{1}H–NMR spectra, there was 0.1 mol% double bonds in these copolymers. This information combined with the ^{13}C–NMR results, strongly supports the conclusion that HD is incorporated into the ethylene backbone exclusively as five-member rings. The amounts of HD in the copolymer calculated on the basis of the ^{13}C–NMR data are reported in Table 2.

The ratio of *cis* and *trans* conformers of the rings affects the properties of the product. Cyclopentane rings in the *cis* conformation are reported to offer high heat stability [26]. In all our copolymers, about 25% of the rings were in *cis* conformation and about 75% in *trans* conformation, and the material obtained had significantly lower melt temperatures than homopolyethylene produced under the same conditions (Table 1). The degree of *cis* rings should thus be higher in order to obtain the crystallinity needed for higher heat stability.

As can be seen from Fig. 2, significant amounts of vinylic chain ends as well as *trans*-vinyl bonds and vinylidene groups were present in the ethylene/OD copolymers. The lines at 5.9 and 4.9 ppm are assigned to vinyl groups, and those at 4.8 and 5.9 ppm to vinylidene and *trans*-vinyl double bonds, respectively. Vinyl bonds are formed when the diene is incorporated to polyethylene by 1,2-addition and the other double bond of the diene remains at the end of the hexene branch end or alternatively at the polyethylene chain end reaction. *Trans*-vinyl and vinylidene bonds are probably formed via β–H elimination at the diene inserted propagation end.

^{13}C–NMR studies showed that OD forms both single branches and branch pairs to the polyethylene backbone. From this, we concluded that every OD unit in the copolymer contains a double bond and thus the OD content of the product can be calculated from ^{1}H–NMR spectra (Table 2). The diene content in the product had no clear effect on the relative amounts of different double bonds in the copolymer. From 60 to 65% of the double bonds in the copolymers were vinylic; the amount of vinylidene bonds was about 30% and the rest were *trans*-vinyl bonds. The conversion of OD was about 20%.

MOD is polymerized with ethylene via its unsubstituted double bond. The branches that are formed have a $RCH{=}CMe_2$ (dimethylvinyl) end, which gives a line at 5.1 ppm in the ^{1}H–NMR spectrum. About 30 to 50% of the double bonds in our ethylene/MOD samples were as these while 30–45% were vinyl bonds. The relatively large amount of vinyl bonds can be explained by the small amount of incorporated MOD and low molar mass of the copolymer. The amount of diene in the product remained under 0.5 mol% for all diene concentrations in the reactor (Table 2) and the conversion of MOD decreased from 4 to 0.4% when diene concentration in the reactor was increased. The diene content of these ethylene/MOD copolymers is

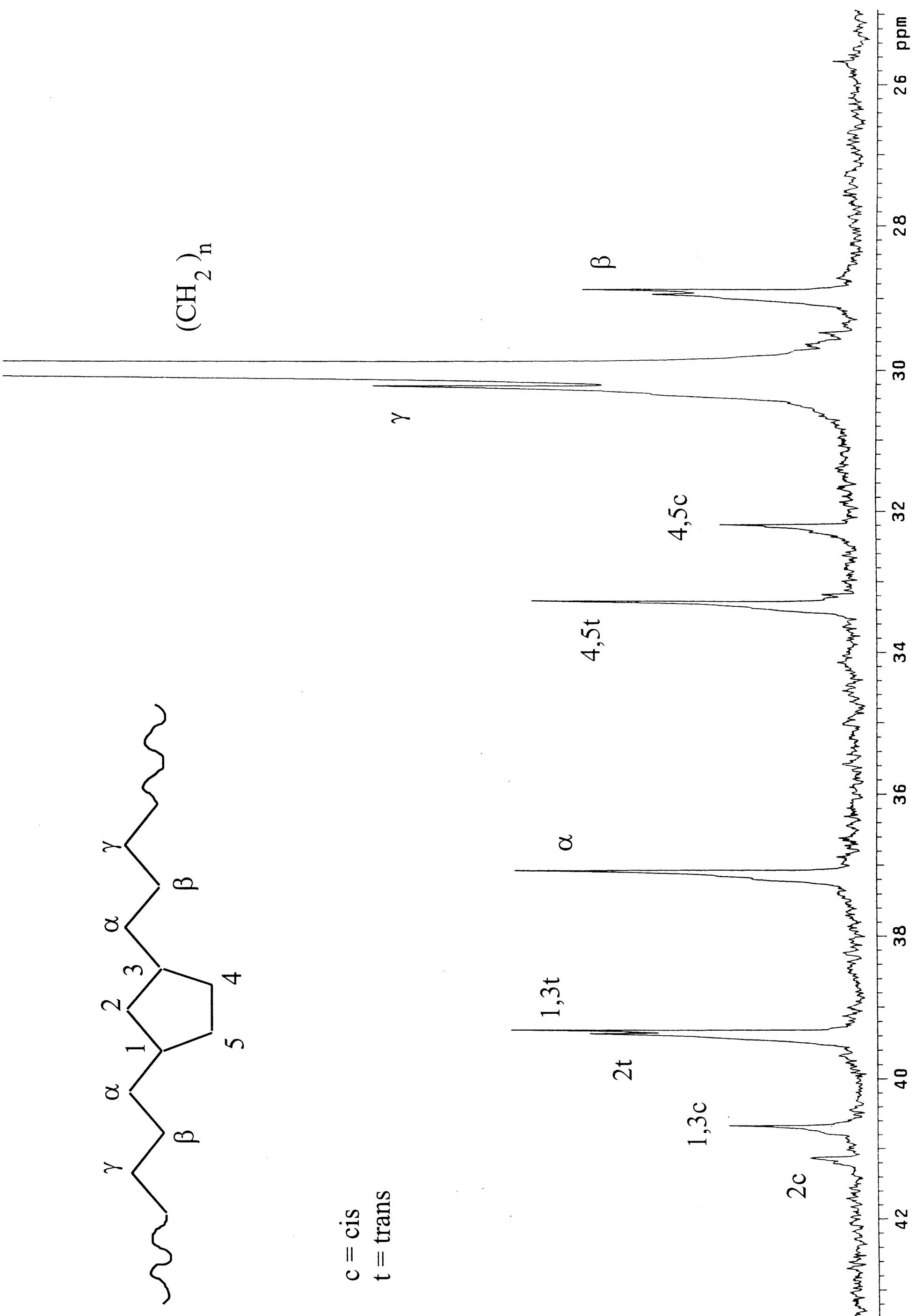

Fig. 1. ^{13}C–NMR (300 MHz) spectra of ethylene/1,5-hexadiene copolymer (sample 3) dissolved in 1,1,2,2-tetrachloroethane-d_2 at 125°C. Sample was prepared with catalyst system Cp_2ZrCl_2/MAO at 90°C.

Table 2
Diene content of ethylene/1,5-hexadiene (HD), ethylene/1,7-octadiene (OD) and ethylene/7-methyl-1,6-octadiene (MOD) copolymers determined by NMR[a]

Sample	Diene in the reactor, mol/dm^3	Diene in the product by ^{1}H–NMR		^{13}C–NMR		Double bond concentration by FTIR per 1000 C		
		mol%	wt%	mol%	wt%	*trans*-vinyl	vinyl	vinylidene
1	—	0	0	0	0	0.33	0.99	0.07
HD								
2	0.02			1.1	3.2	0.23	0.52	0.04
3	0.06			2.8	7.8	0.24	0.54	0.17
4	0.36			7.5	19.3	0.45	0.36	n.d.
OD								
5	0.01	0.7	2.8			0.43	2.84	1.28
6	0.04	1.3	5.1			0.58	4.75	2.13
7	0.27	3.7	13.2			0.90	10.79	3.47
MOD								
8	0.04	0.2	0.8			0.42	0.54	0.75
9	0.12	0.3	1.3			0.83	0.55	1.92
10	0.48	0.5	2.1			1.19	0.50	2.56

[a] The amount of HD is calculated on basis of five-member rings in the product by ^{13}C–NMR and the amount of octadienes on the basis of double bonds in the product determined by ^{1}H–NMR. 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 [HD] > 0.4); polymerization time 15 min.

low compared with those containing OD, which is understandable, since OD has polymerizable double bonds at both ends and MOD only at one end.

3.2. *FTIR study of the copolymer structure*

The appearance of double bonds in ethylene/diene copolymers was also studied by FTIR spectrometry, a method that is extremely sensitive even for low double bond concentrations. Detected wave numbers of the double bonds studied were 965 cm^{-1} (*trans*-vinyl), 910 cm^{-1} (vinyl) and 888 cm^{-1} (vinylidene). Fig. 3 shows an example of the appearance of double bonds in the FTIR spectrum of our ethylene/diene copolymers.

Table 2 reports the double bond concentrations of the copolymers as a function of diene addition. The increase in total double bond concentration with diene concentration in the polymerization is clearly seen for the ethylene/OD copolymers. The high vinyl bond concentration is due to the hexene branches formed by OD and low molar mass of the product. The increase of comonomer also increased the amount of vinylidene bonds in the product because the probability of primary insertion of the comonomer is very high [31].

Increasing amounts of diene had a minor effect on the double bond concentration of ethylene/HD copolymers and ethylene/MOD copolymers: the *trans*-vinyl and vinylidene concentrations, but not the vinyl concentration, were increased with the amount of diene in the product. The vinyl bond concentration was decreased with an increasing diene portion in HD containing copolymers because of the efficient ring formation reaction that occurred and consumed the free double bonds of the diene. As can be seen (Table 2) vinyl bond concentration was lower in copolymers containing HD and MOD than in homopolyethylene produced under the same conditions. This indicated the change of reaction mechanism from β–H elimination to chain transfer to monomer as the chain end reaction.

Comparison of the ^{1}H–NMR and FTIR results reveals the greater sensitivity of FTIR, especially for the of HD containing copolymers. With ^{1}H–NMR, no change could be detected in the amounts of diene in the product with increasing diene concentration, whereas the FTIR results showed slight increases in the *trans*-vinyl and vinylidene concentrations. It needs to be added at the same time that FTIR is not an efficient method to study ethylene/MOD copolymers. Bonds of RCH=CMe$_2$ type that would appear in these copolymers cannot be detected by FTIR because they are overlapped by the peak of CH$_2$ oscillations of the polyethylene chain.

Cyclic structures are principally studied by ^{13}C–NMR, but some evidence of them can also be obtained by FTIR. In detailed study of the double bond area in the FTIR spectrum of ethylene/diene copolymers we found the peaks at 945 cm^{-1} and 875 cm^{-1} to increase with the amount of HD (Fig. 4). The same was not found for the other dienes. Evidently, these peaks are due to the five-member rings in the polyethylene chain: the oscillations of CH$_2$ bonds on the ring give peaks at these wave numbers. As also is evident in Fig. 4, the

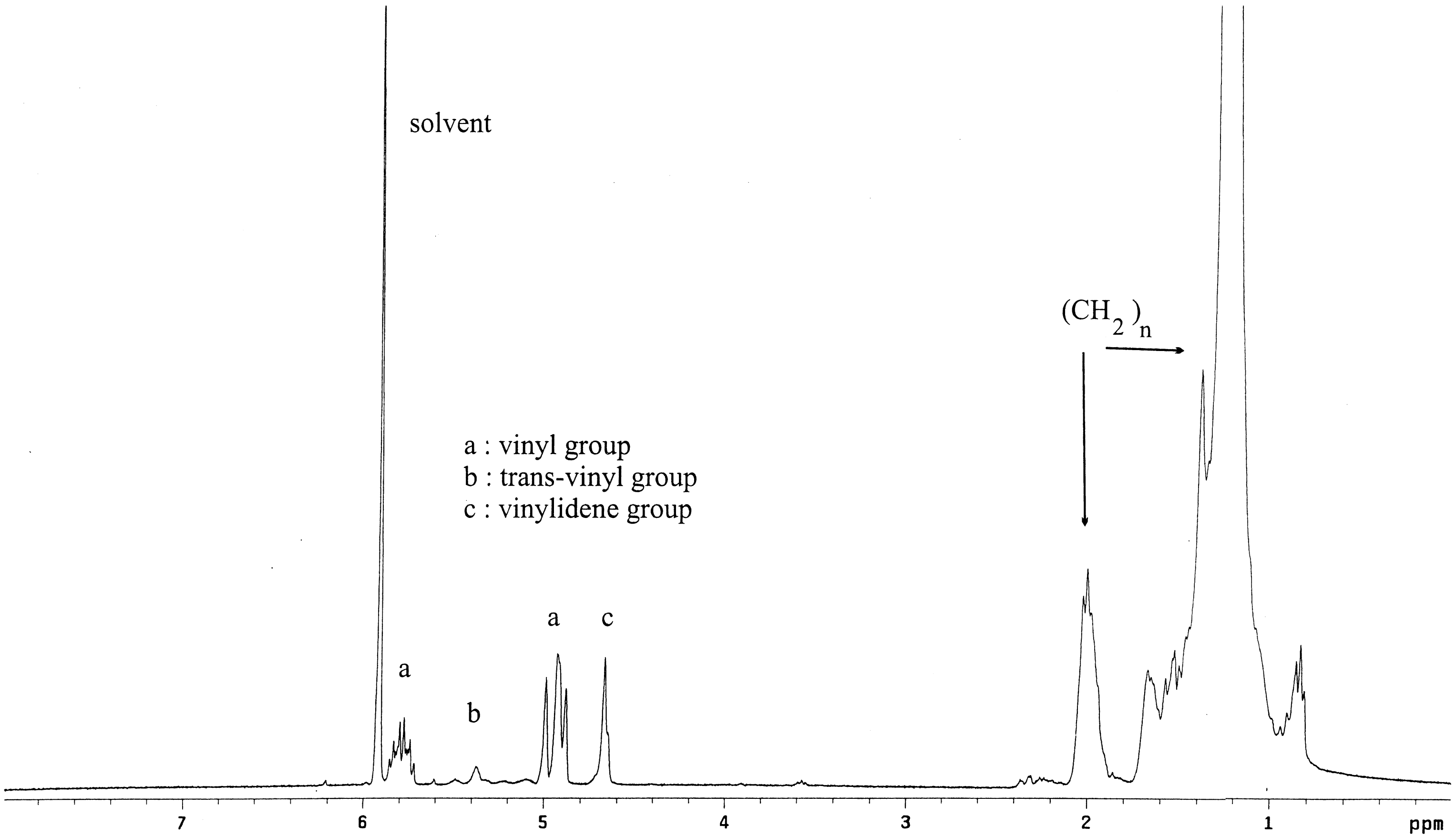

Fig. 2. ^{1}H–NMR (300 MHz) spectra of ethylene/1,7-octadiene copolymer (sample 6) recorded in 1,1,2,2-tetrachloroethane-d_2 at 125°C. Sample was prepared with catalyst system Cp_2ZrCl_2/MAO at 90°C.

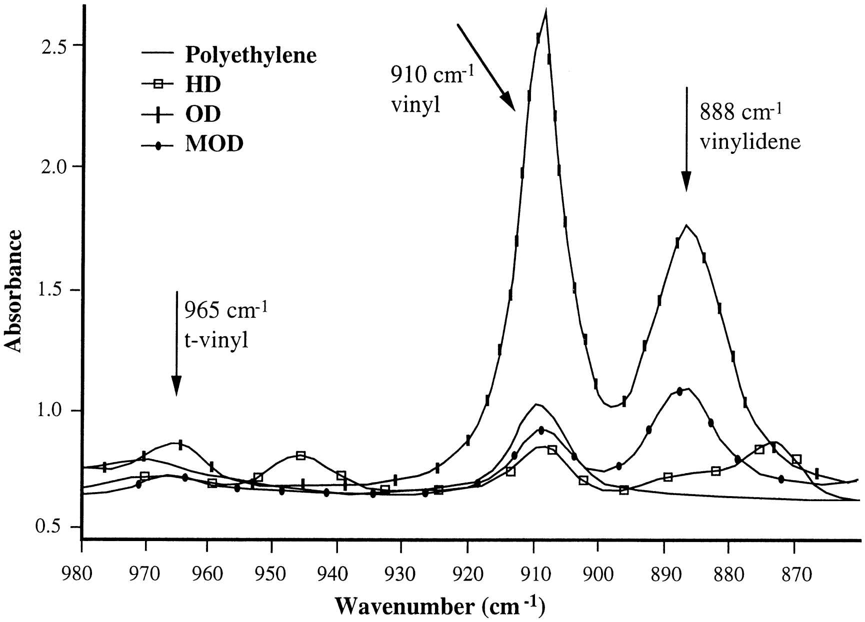

Fig. 3. Comparison of incidence of double bonds by FTIR (*trans*-vinyl 965 cm^{-1}, vinyl 910 cm^{-1} and vinylidene 888 cm^{-1}) in ethylene copolymers with different dienes. Samples (1, 3, 6, 9) were prepared using catalyst system Cp_2ZrCl_2/MAO at 90°C. HD = 1,5-hexadiene, OD = 1,7-octadiene, MOD = 7-methyl-1,6-octadiene.

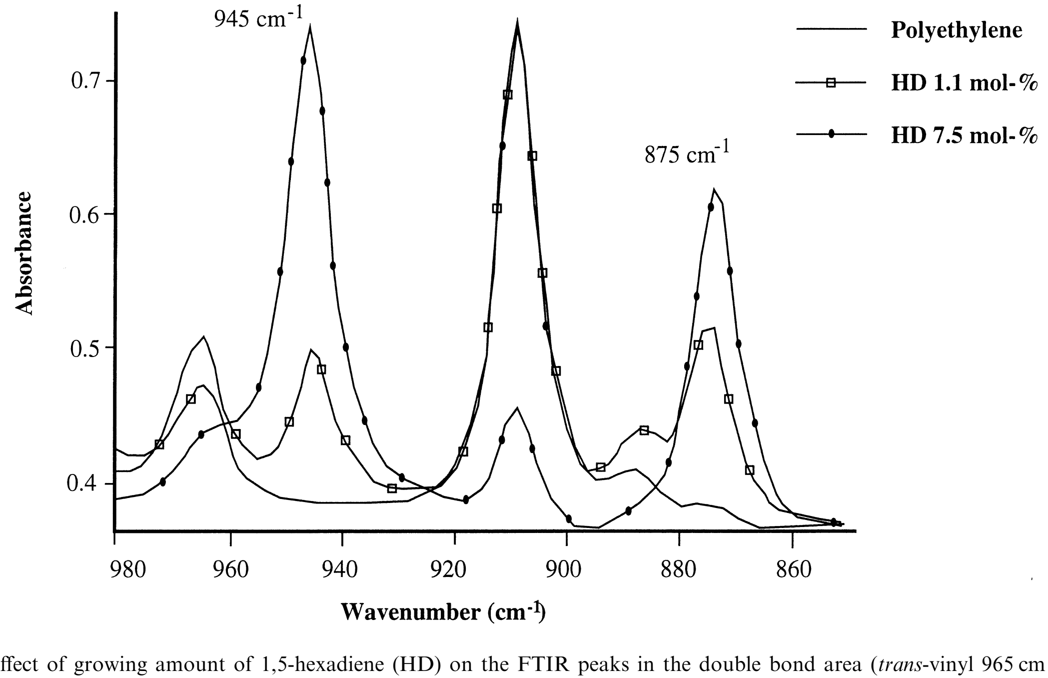

Fig. 4. Effect of growing amount of 1,5-hexadiene (HD) on the FTIR peaks in the double bond area (*trans*-vinyl 965 cm^{-1}, vinyl 910 cm^{-1}, vinylidene 888 cm^{-1} as well as 945 cm^{-1} and 875 cm^{-1}). Samples (2, 3, 4) were prepared using catalyst system Cp_2ZrCl_2/MAO at 90°C.

intensities of the peaks of vinyl, *trans*-vinyl and vinylidene bonds decrease with increasing HD addition.

For OD containing copolymers, both ^{1}H–NMR and FTIR methods reveals a clear increase in the amount of double bonds when the diene concentration in the reactor was increased. The ratios between the different double bonds were the same too, which indicates successful determination of base lines in the FTIR spectra.

3.3. Properties of the product

Crystallinity and melting point decreased significantly as the diene content of the product was increased. Even a small amount of diene in the copolymer caused a drop in crystallinity from 63 to 39% and of melt temperature from 134 to ca. 125°C (Table 2). OD and MOD seemed to have a stronger effect than did HD on both properties even though HD is incorporated in the polyethylene chain at a higher rate. This indicates that branches with vinylic bonds or a RCH=CMe$_2$ end have a more disturbing effect on the crystal structure than do the rings formed by HD. In fact the effect of rings on crystallinity and melt temperature was very small compared with the effect of smaller amounts of OD and MOD branches in the product.

According to Table 1 the activity of the catalyst clearly decreased with increasing MOD content. Same trends in the activity were not seen for HD or OD copolymerizations. Increased amount of HD had hardly any effect on the molar mass and polydispersity of the product, while increasing amount of OD and MOD in the product decreased the molar mass and increased the polydispersity of the product. Especially in the case of OD the increase of polydispersity from 2.8 to 6.7 is a sign of strongly branched structure. Surprisingly, the degree of crosslinking was at a low level for all our copolymers. A strong tendency of OD to form crosslinks would have been expected because of the large amount of vinyl bonds in the copolymer, but under our experimental conditions the degree of crosslinking was less than 0.7%. In HD-containing copolymers the lack of crosslinking is due to ring formation that uses up the vinyl bonds of the diene, and in ethylene/MOD copolymers the methyl group at the one end prevents this double bond from crosslinking.

4. Conclusions

Dienes are effectively incorporated to polyethylene by metallocene catalysts and they have a significant effect on the properties of the polyethylene chain. HD is incorporated in the form of five-member rings with a conversion of 25–40%. It can be thought that these rings might produce interesting properties to the polyethylene by making the chain more rigid if the amount of the HD in the product would be large enough. Also the *cis–trans* relation of the cyclopentane rings affects the melting behaviour of the copolymer. An appreciable amount of HD in the product had only a minor effect on the molar mass, however. On the other hand, even small amounts of OD and MOD in the product decreased the crystallinity and the melt temperature of the product significantly. This shows that the five-member ring structure in the polyethylene chain disturbs the regularity of the structure less than do hexene and 1-methyl-hexene branches. Of the three dienes studied, MOD affected the polymerization most. Despite the low incorporation of MOD, the molar mass, the crystallinity and the melt temperature of the product decreased drastically, as a consequence of the decreased molar mass of the product.

FTIR showed greater sensitivity than ^{1}H–NMR in the determination of the amounts of double bonds in the polymer, giving more detailed information on the low double bond concentrations of HD and MOD containing copolymers. The appearance of double bonds could also be detected by FTIR because the CH$_2$-group of the five-carbon ring produces oscillations at 875 cm^{-1} and 945 cm^{-1}.

Further studies will be carried out on the effect of temperature and catalyst structure on the ring formation and the incorporation of octadienes into the polyethylene chain. Potential long chain branching is being studied by rotational rheometer.

References

[1] Kaminsky W, Bark A, Spiehl R, Neiboda N. In: Kaminsky W, Sinn H, editors. Proceedings, International Symposium on Transition Metals and Organometallics as Catalysts for Olefin Polymerization. Berlin: Springer, 1988. p. 291.
[2] Welborn HC Jr. Wo. pat. 8804672, App. 19.12.1986, Acc. 30.6.1988.
[3] Welborn HC Jr. Wo. pat. 8804674, App. 19.12.1986, Acc. 30.6.1988.
[4] Floyd S, Hoel EL. Eur. pat. 347129, App. 9.6.1989, Acc. 20.12.1989.
[5] Kaminsky W, Dögermyller H. Makromol Chem, Rapid Commun 1990;11:89.
[6] Etheronton BP, Huff T. Wo. pat 9117194, App. 7.5.1991, Acc. 14.11.1991.
[7] Galimberti M, Albizzati E, Abis L, Bacchilega G. Makromol Chem 1991;192:2591.
[8] Yu Z, Marques M, Rausch D, Chien JCW. J Pol Sci, Part A 1995;33:979.
[9] Kaminsky W, Miri M. J Pol Sci, Pol Chem Ed 1985;23:2151.
[10] Kresge EN, Datta S. Eur pat. 227206, App. 1.8.1986, Acc. 1.7.1987.

[11] Kaminsky W, Spiehl R. Makromol Chem 1989;190:515.

[12] Chien CW, He D. J Pol Sci, Part A 1991;29:1609.

[13] Kaminsky W, Bark A, Arndt M. Makromol Chem, Macromol Symp 1991;47:83.

[14] Marathe S, Sivaram S. Macromolecules 1994;27:1083.

[15] Chung TC, Lu HL, Li CL. Macromolecules 1994;27:7533.

[16] Lee D-H, Yoon K-B, Park J-R, Lee B-H. Eur Polym J 1997;33:447.

[17] Resconi L, Waymouth R. J Am Chem Soc 1990;112:4953.

[18] Coates GW, Waymouth RM. J Am Chem Soc 1991;113:6270.

[19] Resconi L, Coates GW, Mogstad A, Waymount RM. J Macromol Sci-Chem 1991;A28:1225.

[20] Mogstad A-L, Waymouth R. Macromolecules 1992;25:2282.

[21] Resconi L, Mazzocchi R, Piemontesi F. Eur pat 508450, App 10.4.1992, Acc. 14.10.1992.

[22] Cavallo L, Guerra G, Corradini P, Resconi L, Waymouth R. Macromolecules 1993;26:260.

[23] Coates GW, Waymouth RM. J Am Chem Soc 1993;115:91.

[24] Cheng HN, Khasat NP. J Appl Pol Sci 1988;35:825.

[25] Bergemann C, Cropp R, Luft G. Chemie Ingenieur Technik 1996;68:417.

[26] Austin RG, Welborn HC Jr. Wo. pat 88/04673, App. 19.12.1986, Acc. 30.6.1988.

[27] Bergemann C, Cropp R, Luft G. J Molecular Catalysis A: Chemical 1997;116:317.

[28] Haslam J, Willis HA., Squirrell DCM. Identification and Analysis of Plastics, 2nd ed. London: Butterworth, 1972. p. 372.

[29] ASTM D-2765-84. Standard test methods for determination of gel content and swell ratio of crosslinked ethylene plastics.

[30] Miller SA, Waymouth RM. In: Fink G, Mülhaupt R, Brinzinger HH, editors. Ziegler Catalysis. Berlin: Springer, 1995. p. 441.

[31] Resconi L, Fait A, Piemontesi F, Colonnesi M. Macromolecules 1995;28:6667.