

Copolymers of Ethylene with Butene-1 and Long Chain α -Olefins, III. Hexadecene-1 As Long Chain α -Olefin

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Synopsis

Hexadecene-1 was used as comonomer with ethylene in a slurry polymerization with Ziegler-Natta catalysts. Hexadecene contents remained at less than 4 wt % in ethylene/hexadecene-1 copolymers. When butene-1 was also present in the polymerization, hexadecene-1 contents were significantly higher. With hexadecene content of 11 wt %, the terpolymer density was 910 g/dm³. The effect of butene addition was significantly smaller with less than 10 carbon atoms containing α -olefins.

INTRODUCTION

Properties of polyethylene are greatly dependent on main chain branches and their distribution. Branches can be produced by copolymerizing ethylene with α -olefins. Usually less than six carbon atoms containing α -olefins are used in slurry or gas phase processes. Longer α -olefins can be used in solution process.¹⁻³

In Parts I and II,^{4,5} the reactions of decene-1 and dodecene-1 with ethylene in heptane slurry were investigated, and the basic properties of these copolymers studied. It was possible to prepare copolymers containing more than 10 wt % of long α -olefin, when butene-1 was simultaneously added to the reactor. Increasing comonomer content reduced density and crystallinity, whereas main peak melting temperature remained approximately at the typical level for a corresponding ethylene/butene-1 copolymer.

This article concerns the use of hexadecene-1 in terpolymerization with ethylene and butene-1, as well as basic properties of the terpolymers. A comparison of decene-1, dodecene-1, and hexadecene-1 in terpolymerization is made.

EXPERIMENTAL

Polymerizations and product analysis were carried out according to the procedures described previously.⁴ Commercial aluminium-activated titaniumtrichloride was used as the Ziegler-Natta catalyst, and triethylaluminium as cocatalyst in the suspension type polymerizations. The reaction medium was *n*-heptane. Hexadecene-1 concentrations in the reactor at the beginning of the polymerizations were 0.1–1.0 mol/dm³. The highest butene-1 concentrations were 0.5 mol/dm³. Reaction conditions are given in Table I, and compositions and basic physical properties appear in Table II.

TABLE I
Polymerization Reaction Conditions^a

Experiment no.	Catalysts		Monomers			Reaction temperature (°C)
	Et ₃ Al (mmol)	Ti-cat. (mmol)	Ethylene (mol/dm ³)	Butene-1 (mol/dm ³)	Hexadecene-1 (mol/dm ³)	
1	4.0	1.8	0.20	—	0.48	95
2	4.8	0.5	0.25	—	0.50	90
3	5.2	2.4	0.40	—	0.48	88
4	5.7	0.6	0.30	—	1.0	90
5	4.9	2.2	0.35	0.03	0.48	90
6	4.1	1.9	0.40	0.06	0.48	88
7	4.1	1.9	0.45	0.18	0.48	90
8	2.9	1.3	0.45	0.48	0.12	90
9	2.9	1.3	0.30	0.48	0.24	90
10	2.6	1.2	0.40	0.48	0.48	89
11	4.2	0.8	0.27	0.50	0.50	90
12	7.5	1.1	0.27	0.50	0.50	90
13	4.8	0.6	0.48	0.50	0.50	90

^a All polymerizations were done with a hydrogen partial pressure of 300 kPa and a reaction time of 2 h.

TABLE II
Polymer Compositions and Basic Properties

Experiment no.	Ethyl branches/100C	Butene-1 content (wt %)	Hexadecene-1		T_m (°C)	Crystallinity (%)	Density (g/dm ³)	\bar{M}_v (10 ⁵) g/mol	$\frac{\bar{M}_w}{\bar{M}_n}$
			Branches/100C	content (wt %)					
1	—	—	0.3	4.0	130	60	941	1.5	9.5
2	—	—	0.2	3.5	134	66	955	1.3	9.0
3	—	—	0.1	2.0	130	62	941	1.9	7.8
4	—	—	0.3	4.3	134	66	951	1.6	10
5	0.2	0.5	0.3	4.5	128	61	939	1.3	8.0
6	0.3	1.0	0.3	5.1	128	52	934	1.5	9.1
7	0.5	1.8	0.4	6.1	127	47	928	1.3	8.6
8	1.7	6.1	0.2	3.9	125	40	918	1.1	6.0
9	2.0	6.8	0.9	12	124	27	905	1.7	6.4
10	1.5	5.1	0.8	11	125	39	909	0.6	6.9
11	2.7	8.0	2.0	23	123	20	890	0.5	4.6
12	2.3	7.3	1.8	22	120	<20	890	0.4	4.0
13	1.6	5.5	0.8	12	123	36	912	0.8	6.8

RESULTS

The reaction of hexadecene-1 could be determined and the compositions measured from ^{13}C -NMR spectra according to the methods described previously.⁴ Resonances typical for six or more carbon atoms containing branches⁶ could be identified in ^{13}C -NMR spectra; typical spectra are shown in Figure 1. Up to 2.0 long branches per 100 main chain carbon atoms were determined in the samples, corresponding to about 23 wt % hexadecene-1 content in the copolymer. Butene-1 addition improved the reactivity of hexadecene-1, as was previously detected for decene-1 and dodecene-1. In the absence of butene-1, hexadecene-1 content in polymer remained at less than 0.3 side chains per 100 main chain carbon atoms, corresponding to less than 4 wt %.

In the DSC curves (Fig. 2), a melting range at about 100°C was noted in the terpolymer samples with high hexadecene-1 contents. This melting range was previously observed for terpolymers containing high contents of decene-1 and dodecene-1,^{4,5} and is an indication of a heterogeneous structure of the copolymers. The DSC curve of ethylene/hexadecene-1 copolymer is narrow and melting temperature high compared to ethylene/butene-1/hexadecene-1 terpolymers. Figure 3 shows that hexadecene-1 content did not have an effect on the main peak temperature of the DSC curve. The melting temperature was consistently 124–125°C in terpolymer samples.

Crystallinities were reduced substantially by increasing hexadecene-1 contents in the terpolymers. A hexadecene-1 content of 12 wt % yielded crystallinity of less than 30%. The relation of crystallinity to hexadecene-1 content is shown in Figure 4.

Density reduction with increasing comonomer content is shown in Figure 5. With hexadecene-1 content of more than 10 wt %, density was less than 910 g/dm³, whereas density of correspondingly polymerized ethylene/butene-1 copolymer was 929 g/dm³. Note that, although density decreased, the main melting peak temperature remained nearly constant at 125°C.

The effect of butene-1 concentration on the reactivity of hexadecene-1 was studied by changing the amount of butene-1 added to the reactor. The ethylene concentration in the reactor was 0.35–0.45 mol/dm³, the hexadecene-1 concentration 0.5 mol/dm³, and the polymerization temperature 90°C. Figure 6 shows that increasing butene-1 concentration in the reactor substantially raises hexadecene-1 content in the terpolymer. The biggest relative increment is in the range of small butene-1 concentrations; adding 0.2 mol/dm³ butene-1 to the reactor increased hexadecene-1 content in the terpolymer from 2 wt % to 6 wt %. The butene-1 contents measured from the terpolymers were similar to those of correspondingly prepared ethylene/butene-1 copolymers.

DISCUSSION

Parts I and II^{4,5} report that butene-1 has a similar effect on the reactivity of decene-1 and dodecene-1 as in this study has been detected on the reactivity of hexadecene-1 (see Fig. 7). Butene-1 addition mainly affects the reaction of decene-1 and longer α -olefins, has a small effect on the reactivity

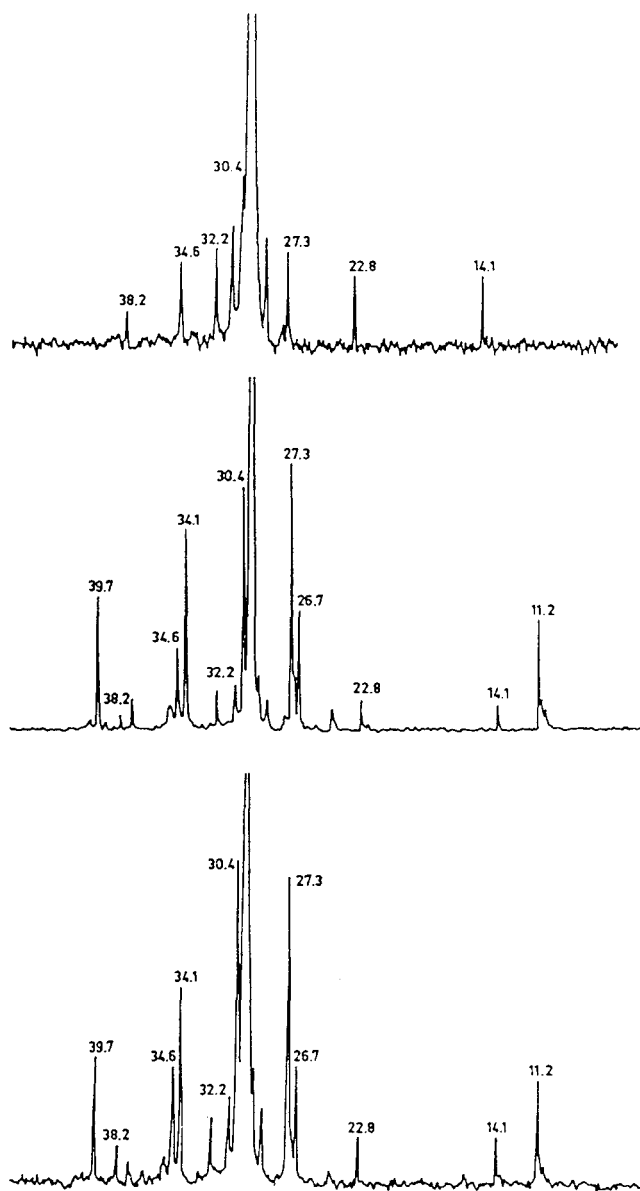


Fig. 1. Typical ^{13}C -NMR spectra of copolymers. Resonances indicated as ppm TMS: (a) ethylene/hexadecene-1 copolymer (experiment no. 3); (b) ethylene/butene-1/hexadecene-1 copolymer (experiment no. 9); (c) ethylene/butene-1/hexadecene-1 copolymer (experiment no. 10).

of octene-1, and has practically no effect on the reactivity of hexene-1. A small addition of butene-1 seems to substantially change copolymerization behaviour of long α -olefins. Thus, it is possible to produce in slurry terpolymers of ethylene having densities of less than 910 g/dm^3 , when the long α -olefin content exceeds 10 wt %. The densities of corresponding butene-1 content having ethylene/butene-1 copolymers were about 929 g/dm .

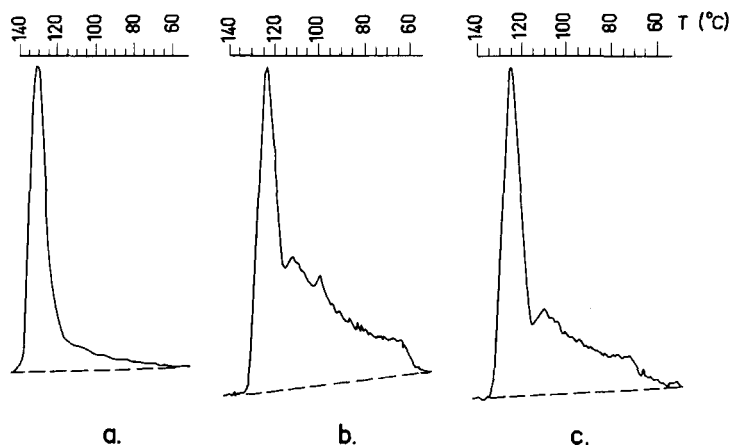


Fig. 2. Typical DSC curves of prepared copolymers: (a) ethylene/hexadecene-1 copolymer (experiment no. 3); (b) ethylene/butene-1/hexadecene-1 copolymer (experiment no. 9); (c) ethylene/butene-1/hexadecene-1 copolymer (experiment no. 10).

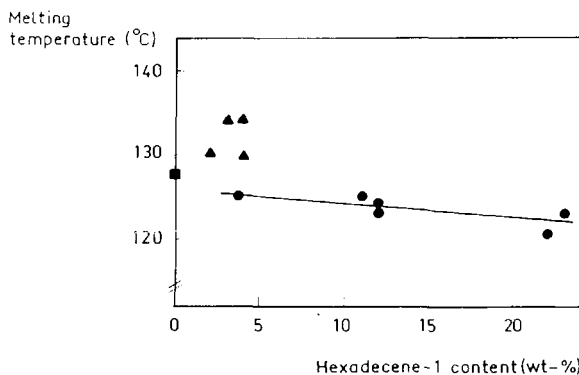


Fig. 3. Dependence of copolymer melting temperature on hexadecene-1 content. (●) ethylene/butene-1/hexadecene-1 copolymer (butene content 6–8 wt %); (■) ethylene/butene-1 copolymer (butene content 6–8 wt %); (▲) ethylene/hexadecene-1 copolymer.

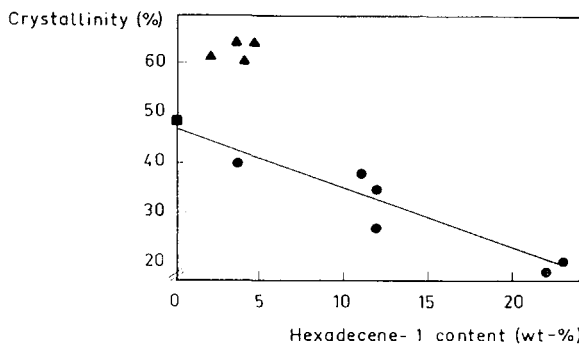


Fig. 4. Effect of decene-1 content of copolymers on crystallinity. Symbols are explained in Figure 3.

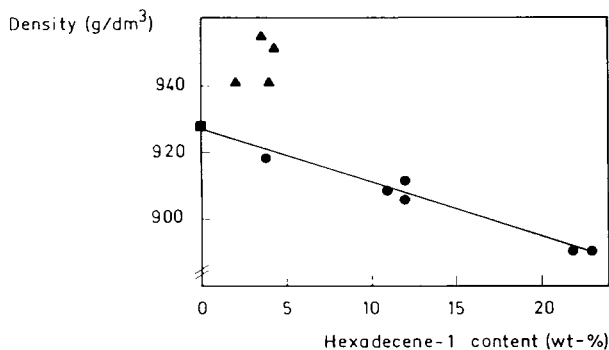


Fig. 5. Dependence of copolymer density on hexadecene-1 content. Symbols are explained in Figure 3.

Figure 8 indicates the substantial change in polymer density caused by butene-1 addition (0.5 mol/dm^3) to the reactor. The copolymers have been prepared in the following conditions: ethylene concentration 0.5 mol/dm^3 , long α -olefin concentration 0.5 mol/dm^3 , and reaction temperature 90°C . The reduction of density by the addition of butene-1 to the reactor was noted for all the long α -olefins used. Octene-1 and hexene-1 used as termonomers produced the smallest reduction. The density reduction of copolymers containing C_{10} – C_{16} α -olefins is substantial because butene-1 addition produces 1–2 ethyl branches per 100 main chain carbon atoms to the copolymer, and causes additionally an increment of long chain α -olefin content.

Pyrolysis hydrogenation gas chromatography analysis indicated the presence of structures, where the branches caused by butene-1 and long α -olefin are located near each other in the polymer chain.⁷ It has been postulated that butene-1 enables a better reaction of long α -olefins by temporarily removing sterical hindrances.

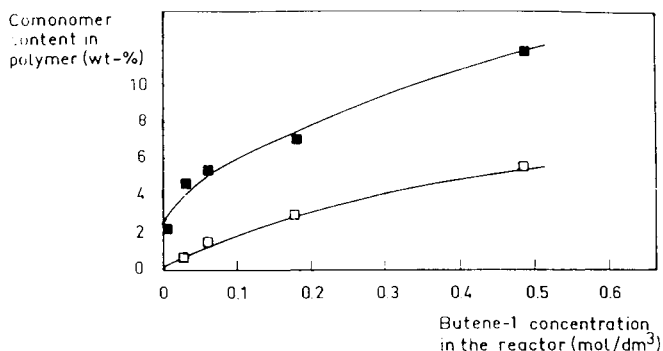


Fig. 6. Effect of butene-1 concentration in the reactor on comonomer content measured from the terpolymers. Polymerization temperature was 90°C and hexadecene-1 concentration in the reactor was 0.48 mol/dm^3 , and ethylene concentration $0.40 \pm 0.05 \text{ mol/dm}^3$: (□) butene-1 content; (■) hexadecene-1 content.

Content of long chain α -olefin in polymer (wt-%)

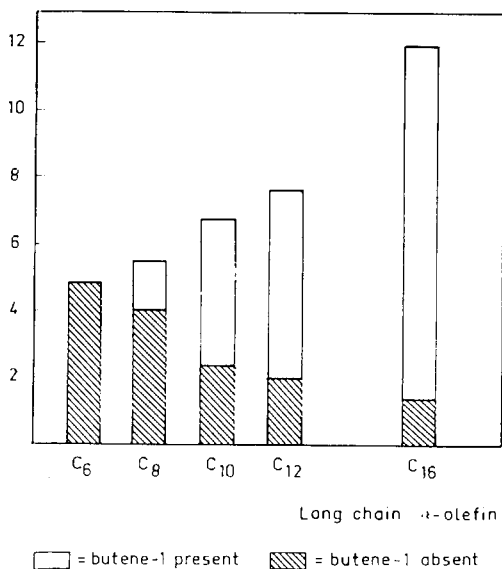


Fig. 7. Effect of butene-1 addition on long chain α -olefin content in copolymers, when different α -olefins were used. Reaction conditions: [ethylene] = 0.5 mol/dm³; [butene] = 0.5 mol/dm³; [long chain α -olefin] = 0.5 mol/dm³.

Kissin's study⁸ would seem to support this. Kissin studied the relative reactivities of different monomer pairs and noted the important role of the last reacted monomer. He reported that chains with small branches in a β position to the end CH₂ group increase the reactivity of certain monomers compared to their reactivity in a homopolymerization reaction. Our study indicates that a similar effect may also be valid for terpolymerizations.

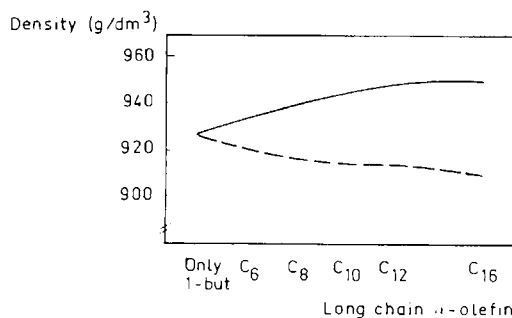


Fig. 8. Effect of butene-1 addition (0.5 mol/dm³) on copolymer density when different α -olefins were used. Reaction conditions: [ethylene] = 0.5 mol/dm³; [long α -olefin] = 0.5 mol/dm³; temperature 90°C; (—) density without butene-1; (---) density with butene-1.

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