

Copolymers of Ethylene with Butene-1 and Long Chain α -Olefins. I. Decene-1 as Long Chain α -Olefin

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Synopsis

The possibility was studied of using decene-1 as comonomer with ethylene in a slurry type polymerization with Ziegler-Natta catalysts. Under the reaction conditions used decene contents remained at the 2 wt % level in ethylene/decene-1 copolymers. When additionally butene-1 was present in the polymerization, decene-1 contents were significantly higher. A synergistic effect was identified in the reactivities of butene-1 and decene-1 in terpolymerization with ethylene. The comonomer reactions were determined and comonomer contents measured by ^{13}C -NMR spectroscopy. Decene-1 content had an effect on the polymer density and crystallinity, but virtually no effect on melting temperature. With high comonomer contents an additional melting range was identified in DSC curves at about 100°C.

INTRODUCTION

High pressure polyethylene typically has 0.5–5 long chain branches per 1000 carbon atoms in the molecule. At a density of about 920 g/dm³ it has 10–20 short chain branches per 1000 carbon atoms. Most of these are butyl branches, but amyl, some methyl, geminal dimethyl, and ethyl branches may be present as well.¹ Several of the characteristic properties of LDPE produced by free radical catalysts are due to the long chain branches, and it can reasonably be assumed that at least some of these properties can be produced in polyethylene grades polymerized with organometallic compounds by using comonomers that produce longer branches. Viscosity properties of solutions and melts of ethylene/ α -olefin copolymers are mainly influenced by long chain branches, whereas crystallinity, density, crystalline melting temperature, stiffness, hardness, gas permeability, and chemical resistance depend on short chain branches.^{1–5}

The interdependencies of density, crystallinity and crystalline melting temperature of ethylene/ α -olefin copolymers have been widely studied,^{2,6–10} and Flory¹¹ has calculated the crystalline melting temperatures.

Shirayama et al.² have studied the properties of copolymers of ethylene with various α -olefins. Crystallization of different branches containing ethylene copolymers has been studied by Bailey and Walter.¹⁰ The crystallization behavior of α -olefin homopolymers have also been widely studied.^{12–20}

Longer α -olefins react only slowly at 60–90°C, the normal temperature range for the slurry process, and the longer α -olefins, such as octene-1, are seldom used except in solution process. α -Olefins containing more than 10 carbon atoms are rarely used as comonomers.^{21,22}

Reactivities can be increased in slurry process by raising the polymerization temperature, but then solubilization becomes a problem. Hogan et al.²³ have published maximum polymerization temperatures for ethylene homopolymerization carried out in different reaction media. Sinclair⁸ has suggested that production of polyethylene grades of densities less than 920 g/dm³ would be difficult. Solubility problems might be avoided, however, by developing suitable catalysts.^{24,25}

It has been shown that the copolymerization equation can be applied to the copolymerization of ethylene by coordination polymerization process.^{26,27} Böhm²⁸ has derived equations for reaction rates. Relative reactivities of different α -olefins in copolymerization with ethylene are known.²⁹⁻³¹

Terpolymerization of ethylene by slurry process with short and long (more than 10 carbon atoms) α -olefin comonomers at the same time is not a well-known process. In this work we have investigated the possibility of producing copolymers of ethylene with decene-1 and butene-1 in a slurry process. The main properties of the polymers are described.

EXPERIMENTAL

Polymerizations

Polymerizations were carried out in a 4 dm³ semibatch stirred tank reactor. Reaction medium was *n*-heptane. Comonomers, catalysts, and hydrogen were fed to the reactor at the beginning of the polymerization. Reactor pressure was maintained at the desired level with a continuous ethylene feed. The ethylene feed tank was weighed continuously to an accuracy of within ± 1 g.

The catalyst was commercial aluminium-activated TiCl₃, the cocatalyst was Et₃Al, and the molar ratio Ti/Al was 0.5. Polymerizations were carried out at 80 and 90°C. Ethylene partial pressure was maintained at 700 kPa. On the basis of preliminary experiments 0.48 mol/dm³ was selected as the initial concentration for butene-1. Decene-1 concentration in the reactor was between 0.12 and 0.48 mol/dm³, so that the molar ratio butene-1/decene-1 was 4.0-1.0. A slight concentration change occurred with the reaction time because of the batchwise addition of comonomers. To study the effect of butene-1 concentration on the reactivity of decene-1, the concentration of butene-1 was varied in the range 0.03-0.48 mol/dm³. Experiments were also done without butene-1 at both polymerization temperatures. The following copolymers were prepared with the same catalysts and the same experimental conditions to get reference samples: ethylene/butene-1, ethylene/hexene-1, ethylene/octene-1, ethylene/butene-1/hexene-1, and ethylene/butene-1/octene-1. The molecular weight of the polymer was regulated with hydrogen at a partial pressure of 300 kPa. After 2 h polymerization time the reactor pressure was reduced, the reactor cooled, and the slurry removed. The polymer was filtered, washed to remove catalyst residues and dried in a fluid bed drier at 60°C. Between 300 and 600 g of ethylene copolymer product was obtained. The reaction conditions are collected into Table I.

TABLE I
 Polymerization Reaction Conditions^a

Experiment no.	Catalysts		Monomers			<i>T</i> (°C)
	Et ₃ Al (mmol)	Ti-cat. (mmol)	Ethylene (mol/dm ³)	Butene-1 (mol/dm ³)	Long α-olefin (mol/dm ³)	
1	1.7	0.7	0.55	0.48	—	90
2	2.2	1.0	0.50	—	Hexene-1 0.48	90
3	2.8	1.3	0.50	0.48	0.48	91
4	2.4	1.1	0.50	—	Octene-1 0.48	89
5	2.2	1.0	0.50	0.48	0.48	90
6	2.2	1.0	0.50	—	Decene-1 0.48	80
7	1.9	0.9	0.50	—	0.48	89
8	1.5	0.7	0.55	0.03	0.48	89
9	1.6	0.7	0.50	0.06	0.48	90
10	1.6	1.1	0.35	0.18	0.48	90
11	2.4	1.1	0.47	0.48	0.12	90
12	2.6	1.2	0.47	0.48	0.24	80
13	2.7	1.2	0.45	0.48	0.24	90
14	2.0	0.9	0.55	0.48	0.48	82
15	2.5	1.2	0.27	0.48	0.48	90

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

ANALYTICAL METHODS

¹³C-NMR Spectroscopy

The side chains in ethylene copolymers prepared from known α-olefins have been well studied³²⁻³⁶ and these results have then been applied for LDPE side chain determinations.^{32-35,37-40} Side chains of less than 6 carbon atoms in length can be identified by ¹³C-NMR spectroscopy, but not side chains of six or more carbon atoms.³² In the polymerizations carried out in this work only one comonomer producing side chains longer than six carbon atoms was used at a time. Thus the side chain concentrations could be analyzed from ¹³C-NMR spectra.

¹³C-NMR spectra were recorded at the Neste Research Centre with a Jeol FX 90 Q spectrometer. Spectra were run from 20 wt % solvents in trichlorobenzene in 10 mm diameter sample tubes. Hexamethyldisulfoxide was used as the reference substance. The following rules can be applied to the interpretation of resonance peak areas in ethylene copolymer ¹³C-NMR spectra³³:

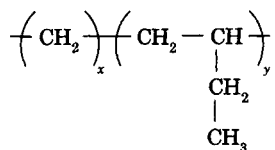
When branches have at least six carbon atoms,

$$\alpha = \beta = \gamma = 3 \times \text{methyl} = 3 \times \text{methine} \quad (1)$$

When branches have less than six carbon atoms,

$$\alpha = \beta = \gamma = 2 \times \text{methyl} = 2 \times \text{methine} \quad (2)$$

The nomenclature used for carbon atoms (Fig. 1) is according to Randall.³³ Ethylene/butene-1 copolymers have the following composition:



Values for x and y can be determined from a ^{13}C -NMR spectrum by using eq. (2) and the equations

$$x = \text{CH}_2 + \frac{1}{2} \alpha + \beta + \gamma \quad (3)$$

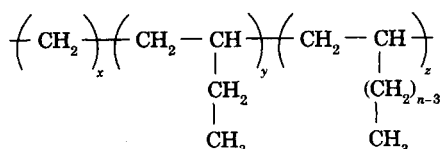
$$y = \frac{1}{2} \alpha = \text{br} = \text{CH}_3 = \text{CH}_2 \text{ of ethyl branch} \quad (4)$$

Further one can determine the number of ethyl branches and the butene-1 content:

$$\text{ethyl branches/100 main chain carbons} = \frac{y}{x + 2y} \times 100 \quad (5)$$

$$\text{butene-1 content in copolymers} = \frac{4y}{x + 4y} \times 100 \text{ wt } \% \quad (6)$$

Terpolymers of ethylene, butene-1, and a long chain α -olefin have the composition



where n is the number of carbon atoms in the long chain α -olefin.

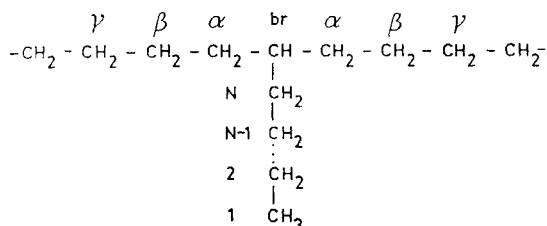


Fig. 1. Nomenclature of carbon atoms in ethylene α -olefin copolymers.

When the prime indicates butene-1 comonomer and the double prime a long chain α -olefin (e.g., decene-1), x , y , and z can be calculated with the following equations, which are derived from eqs. (1) and (2):

$$x = \text{CH}_2 + \frac{\alpha'}{2} + \frac{\alpha''}{3} + (\beta - \text{CH}_3') + (\gamma - \text{CH}_3'') - (n - 8) \times \text{CH}_3'' \quad (7)$$

$$y = \frac{1}{2}\alpha' = \text{CH}' = \text{CH}_3' = \text{CH}_2' \text{ of ethyl branch} \quad (8)$$

$$z = \frac{1}{3}\alpha'' = \text{CH}'' = \text{CH}_3'' \quad (9)$$

Further, the following equations can be derived:

$$\text{ethyl branches/100 main chain carbons} = \frac{y}{x + 2y + 2z} \times 100 \quad (10)$$

butene-1 concentration in the terpolymer

$$= \frac{4y}{x + 4y + n \times z} \times 100 \text{ wt } \% \quad (11)$$

$$\frac{\text{branches produced by long chain } \alpha\text{-olefin}}{100 \text{ main chain carbons}} = \frac{z}{x + 2y + 2z} \times 100 \quad (12)$$

$$\text{long chain } \alpha\text{-olefin concentration} = \frac{z \times n}{x + 4y + n \times z} \times 100 \text{ wt } \% \quad (13)$$

Calorimetry

Differential scanning calorimetry (DSC) curves were obtained from powder samples with a Mettler TA 3000 instrument. Test conditions were: starting temperature -20°C , heating rate $10^\circ\text{C}/\text{min}$, and end temperature 200°C . Crystallinities were determined from melting range integrals using 290 J/g as heat of fusion.

Viscosity Average Molecular Weights

Viscosity average molecular weights were measured according to the standard ASTM D 2857. Decalin was used as solvent at 135°C . The following values were used as Mark-Houwink constants: $K = 62 \times 10^{-3} \text{ cm}^3/\text{g}$, $\alpha = 0.7$.

Molecular weight distributions

Molecular weight distributions were determined by gel permeation chromatography with a Waters 150C ALC/GPC instrument. Trichlorobenzene at 135°C and a flow rate of $1 \text{ cm}^3/\text{min}$ was used as solvent. The instrument had four columns: μ -Styragel 10^3 , 10^5 , 10^6 and 10^6 .

Densities

Polymer densities were measured from compression moulded plates. Measurements were carried out in a gradient column prepared from water/ethanol mixture according to the standard ASTM D 1505.

RESULTS AND DISCUSSION

Branches in the polyethylene structure introduced by the comonomers were identified in ^{13}C -NMR spectra. Figure 2a, b and c shows characteristic spectra for ethylene/butene-1, ethylene/decene-1 and ethylene/butene 1/decene-1 copolymers. Peaks typical for either ethylene/butene-1 copolymers (39.7, 34.1, 30.4, 27.3, 26.7 and 11.2 ppm TMS) or copolymers of ethylene with long α -olefins (38.2, 34.6, 32.2, 30.4, 27.3, 22.8 and 14.1 ppm TMS) were identified in spectra of the ethylene/butene-1/decene-1 terpolymers through reference to the spectra published by Randall³³ for ethylene/ α -olefin copolymers.

The basic chemical and physical properties measured from the polymerization products are recorded in Table II. From this table and (Figure 7) it can be seen that without any butene-1 in the reactor decene-1 concentration in the polymer sample remained at the level of 2 wt %. When butene-1 was added, the decene-1 concentration increased to 13.5 wt %. As a reference, in ethylene copolymerization, when hexene-1 or octene-1 was the comonomer, butene-1 addition had little effect on the concentration of longer α -olefin in the polymer: Hexene-1 comonomer concentration in the polymer was the same whether butene-1 was used or not, and octene-1 comonomer concentration increased only from 4 to 5.7 wt % with the addition of butene-1.

In DSC curves of ethylene/decene-1 copolymers the melting range maximum was over 130°C, which is typical for linear polyethylene [Fig. 3(b)]. In ethylene terpolymers with butene-1 and decene-1 the melting temperatures were 124–130°C [Figs. 3(a) and (c)], and near to those of corresponding ethylene/butene-1 copolymers. When decene-1 content was high, an additional melting range at about 100°C could be detected [Fig. 3(c)]. Figure 4 shows the dependence of melting temperature on decene-1 content in terpolymers prepared with butene-1 concentration of 0.48 mol/dm³ in the reactor.

The DSC curve of ethylene/decene-1 copolymer was like that of ethylene homopolymers. Also crystallinity and density were high. These results support the result obtained by ^{13}C -NMR measurements that decene-1 content in the polymer remains at a low level in the present conditions when decene-1 only is used as comonomer.

The fact that the melting range maximum is always located at 126–128°C in samples with high comonomer contents indicates that regardless of the total composition of the polymer, most crystals have the same composition. Florin et al.⁷ have reported similar behavior for ethylene/hexene-1 copolymers: that independent of hexene concentration the melting temperature is 132°C. However, the appearance of a melting range at 100°C indicates the formation of lower melting crystalline areas in the samples containing high decene-1 contents.

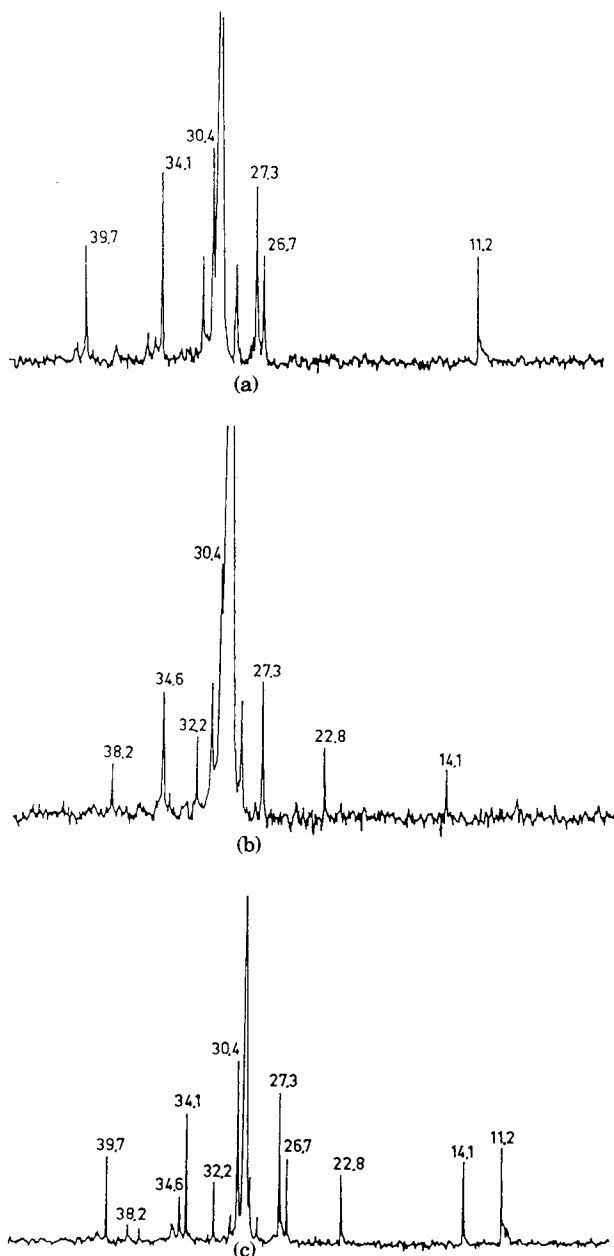


Fig. 2. Typical ^{13}C -NMR spectra of copolymers. Resonances indicated as ppm TMS: (a) ethylene/butene-1 copolymer (experiment no. 1); (b) ethylene/decene-1 copolymer (experiment no. 7); (c) ethylene/butene-1/decene-1 copolymer (experiment no. 15).

The melting range maximum decreased slightly with decrease in density, starting from the melting temperature of the corresponding ethylene/butene-1 copolymers. The melting range maximum of the terpolymers decreased from 128 to 126°C as the density decreased from 930 to 914 g/dm³.

Increased decene-1 content in the polymer markedly reduced the measured crystallinities: from about 50%, which is typical for ethylene/butene-

TABLE II
 Polymer Composition and Basic Properties

Experiment no.	Polymer composition						Crystallinity (%)	Density (g/dm ³)	$\bar{M}_v \times 10^6$ (g/mol)	\bar{M}_w/\bar{M}_n
	Ethyl branches/100 C	Butene-1 concn (wt %)	Longer α -olefin			T_m (°C)				
			Branches/100 C	Concn (wt %)						
1	1.2	5	—	—	—	128	929	1.4	7	
2	—	—	Hexene-1	0.8	4.8	127	933	1.5	7	
3	1.3	5.3	0.8	0.8	4.5	124	915	1.0	7.8	
4	—	—	Octene-1	0.5	3.9	129	936	2.5	8	
5	1.7	6.2	0.8	0.8	5.7	125	917	1.2	7.5	
6	—	—	Decene-1	0.3	2.0	135	946	3.5	7.5	
7	—	—	0.2	0.2	2.3	130	940	2.5	7.0	
8	<1.0	<1.0	0.2	0.2	2.0	133	942	2.5	8.5	
9	0.3	1.0	0.3	0.3	3.3	131	938	2.0	8.2	
10	0.6	2.5	0.7	0.7	6.6	128	929	1.3	7.5	
11	1.2	4.7	0.2	0.2	2.3	124	922	2.0	8.4	
12	1.3	4.9	0.3	0.3	2.7	127	928	1.5	7.6	
13	1.2	4.5	0.5	0.5	4.8	125	921	1.2	7.5	
14	1.2	4.5	0.6	0.6	5.7	127	925	2.0	9.3	
15	1.3	4.5	1.6	1.6	13.5	125	914	1.1	8.0	

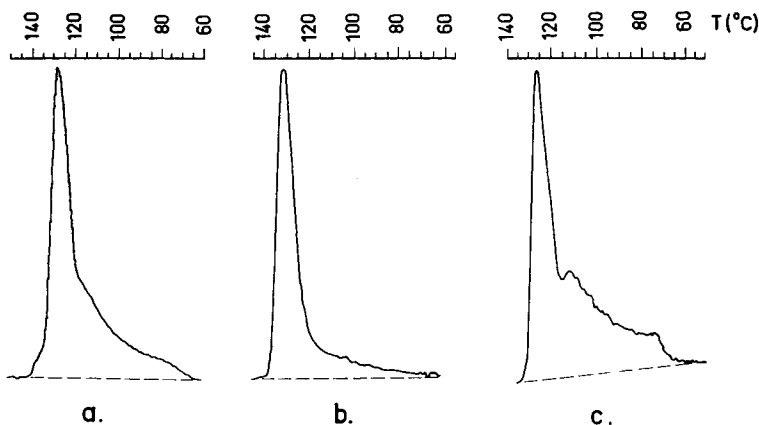


Fig. 3. Typical DSC curves of prepared copolymers: (a) ethylene/butene-1 copolymer (experiment no. 1); (b) ethylene/decene-1 copolymer (experiment no. 7); (c) ethylene/butene-1/decene-1 copolymer (experiment no. 15).

1 copolymer, to less than 40%, when decene-1 content was about 13.5 wt %. In these polymerizations butene-1 concentration in the reactor was constant. A clear correlation between crystallinity and density can be seen in Figure 5.

Figure 6 shows how the density of terpolymers decreases when butene-1 content in the polymerization is maintained constant and decene-1 concentration in the polymer increases. In the sample with 4.5 wt % butene-1 and 13.5 wt % decene-1 the density was 914 g/dm³. In ethylene/butene-1 copolymer having butene-1 concentration of 5 wt % density was 929 g/dm³. The samples polymerized with decene-1 as comonomer, and no butene-1 had densities, crystalline melting temperatures, and crystallinities near to the values of linear HDPE. This was to be expected since the comonomer content in these copolymers remained at a low level.

The plots of the decene-1 content of the copolymer as function of decene-1 concentration in the reactor at the beginning of the polymerization in

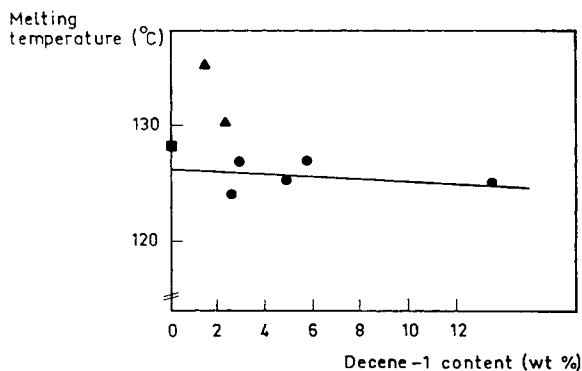


Fig. 4. Dependence of copolymer melting temperature on decene-1 content in the copolymer: (●) ethylene/butene-1/decene-1; (■) ethylene/butene-1 copolymer (butene-1 content 5 wt %); (▲) ethylene/decene-1 copolymer.

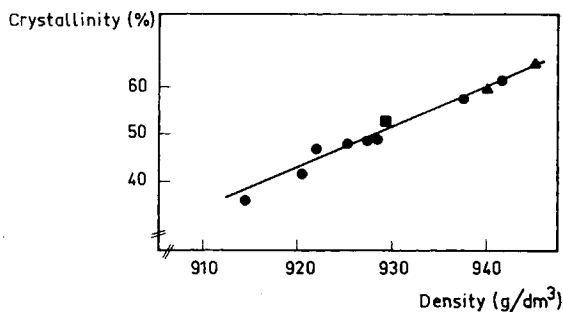


Fig. 5. Dependence of density to crystallinity in copolymers containing decene-1. Symbols are the same which are used in Figure 4; with the exception that butene-1 content is not always the same in ethylene/butene-1/decene-1 copolymers.

Figure 7 show that polymerization temperature has an essential effect on the decene-1 content of the polymer in terpolymerization: temperature change from 80 to 90°C more than doubled the decene-1 contents in the polymer. Temperature increase in that range had no effect, however, when there was no butene-1 in the reactor. In this case decene-1 contents in the polymer remained small.

The effect of butene-1 concentration on the reactivity of decene-1 was studied by changing the amount of butene-1 added to the reactor and otherwise keeping the conditions constant. Figure 8 shows the comonomer contents in the polymers as a function of the initial butene-1 concentration in the reactor. Polymerization temperature was 90°C and decene-1 concentration in the reactor was 0.48 mol/dm³. Increasing butene-1 concentration clearly increased the decene-1 content in the polymer. Butene-1 contents in the terpolymers were near to those of correspondingly prepared ethylene/butene-1 copolymers.

The characteristic values of $\overline{M}_w/\overline{M}_n$ for molecular weight distribution were between 7 and 9 for copolymers containing decene-1. Average molecular weights were lower in polymerizations where butene-1 was present as well. As is well known, butene-1 acts as a chain transfer agent. No reduction in average molecular weights due to decene-1 addition could be detected.

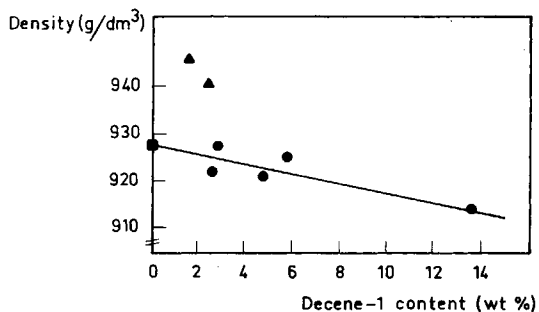


Fig. 6. Dependence of copolymer density on decene-1 content in the polymer. The symbols are explained in Figure 4.

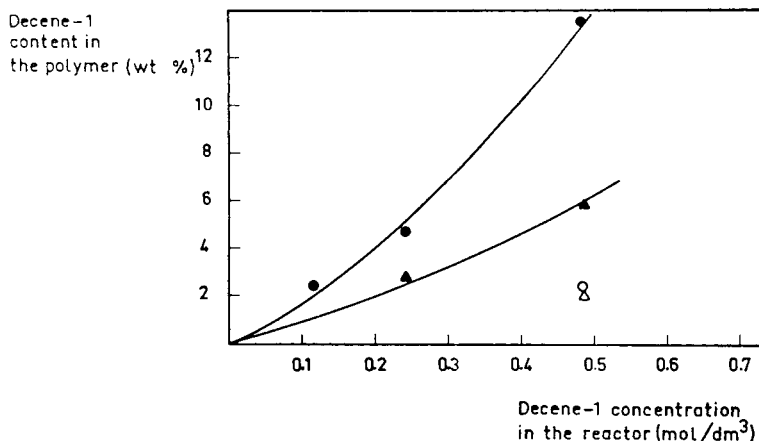


Fig. 7. Effect of initial decene-1 concentration on the decene-1 content obtained in the polymer: (●) ethylene/butene-1/decene-1 copolymer at 90°C; (▲) ethylene/butene-1/decene-1 copolymer at 80°C; (○) ethylene/decene-1 copolymer at 90°C; (△) ethylene/decene-1 copolymer at 80°C.

CONCLUSIONS

The reactivity of decene-1 with ethylene in suspension type coordination polymerization can substantially be increased by adding butene-1 simultaneously into the reactor. Such an effect did not appear in copolymerizations of ethylene with lower α -olefins.

By this method it was possible to prepare terpolymers of ethylene, butene-1 and decene-1 containing more than 10 wt % decene-1. These polymers had low densities and relatively low crystallinities. An additional melting range appeared at 100°C in the samples containing high contents of decene-1.

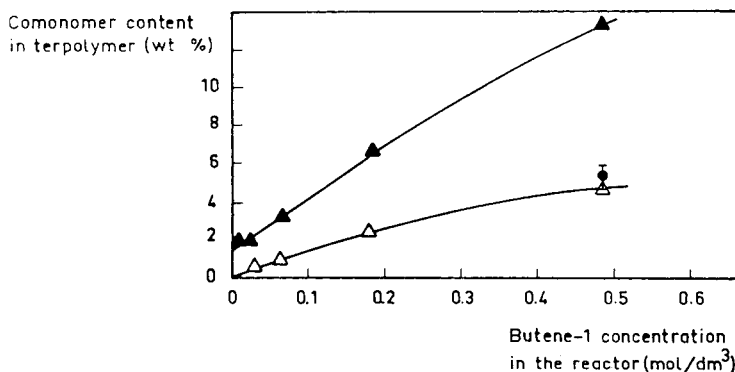


Fig. 8. Effect of initial butene-1 concentration in the reactor on the comonomer contents measured for the terpolymers. Polymerization temperature was 90°C and decene-1 concentration in the reactor 0.48 mol/dm³: (△) butene-1 content; (▲) decene-1 content; (●) corresponding ethylene/butene-1 copolymers.

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