

# Copolymers of Ethylene with Butene-1 And Long Chain $\alpha$ -Olefins. II. Dodecene-1 as Long Chain $\alpha$ -Olefin.

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## Synopsis

Ethylene/dodecene-1 and ethylene/butene-1/dodecene-1 copolymers were prepared and their polymerization reaction in heptane slurry was studied. The Ziegler-Natta catalyst was aluminium-activated  $\text{TiCl}_3$ , and the cocatalyst was triethylaluminium. The dodecene-1 contents in the ethylene/dodecene-1 copolymers were less than 3 wt %. The dodecene-1 contents in terpolymers of ethylene, butene-1, and dodecene-1 ranged up to 10 wt %. The dependence of basic properties on composition of terpolymers was investigated.

## INTRODUCTION

Properties of polyethylene are dependent on branch length and distribution. To produce side chains of polyethylene in suspension or gas phase processes, usually less than 6 carbon atoms containing  $\alpha$ -olefins are used. In solution processes longer  $\alpha$ -olefins may be used.

In Part I,<sup>1</sup> the reaction of decene-1 with ethylene in suspension was discussed. The reaction rate of decene-1 increased, when butene-1 was added simultaneously. In the terpolymers obtained, decene-1 content ranged up to 13.5 wt % when density was  $914 \text{ g/dm}^3$ . The reaction of dodecene-1 in the corresponding system was studied. Investigations of the mechanism and comonomer distribution were also performed.

## EXPERIMENTAL

Polymerizations with dodecene-1 were carried out using the same procedures as reported in Part I.<sup>1</sup> The catalyst was commercial aluminium-activated  $\text{TiCl}_3$ ; the cocatalyst was triethylaluminium.

Dodecene-1 concentration at the beginning of the polymerizations was in the range of  $0.12\text{--}0.73 \text{ mol/dm}^3$ . Polymerizations were carried out at 80 and  $90^\circ\text{C}$ . To study the effects of butene-1 concentrations, initial butene-1 concentration in the reactor was varied between  $0.03$  and  $0.48 \text{ mol/dm}^3$ . Reaction conditions are given in Table I. Analytical methods have been described earlier.<sup>1</sup>

## RESULTS AND DISCUSSION

The  $^{13}\text{C-NMR}$  spectra of typical copolymer samples of ethylene/dodecene-1 and ethylene/butene-1/dodecene-1 appear in Figure 1. Spectra b and c indicate two different comonomer ratios. The reaction of dodecene-1 can be

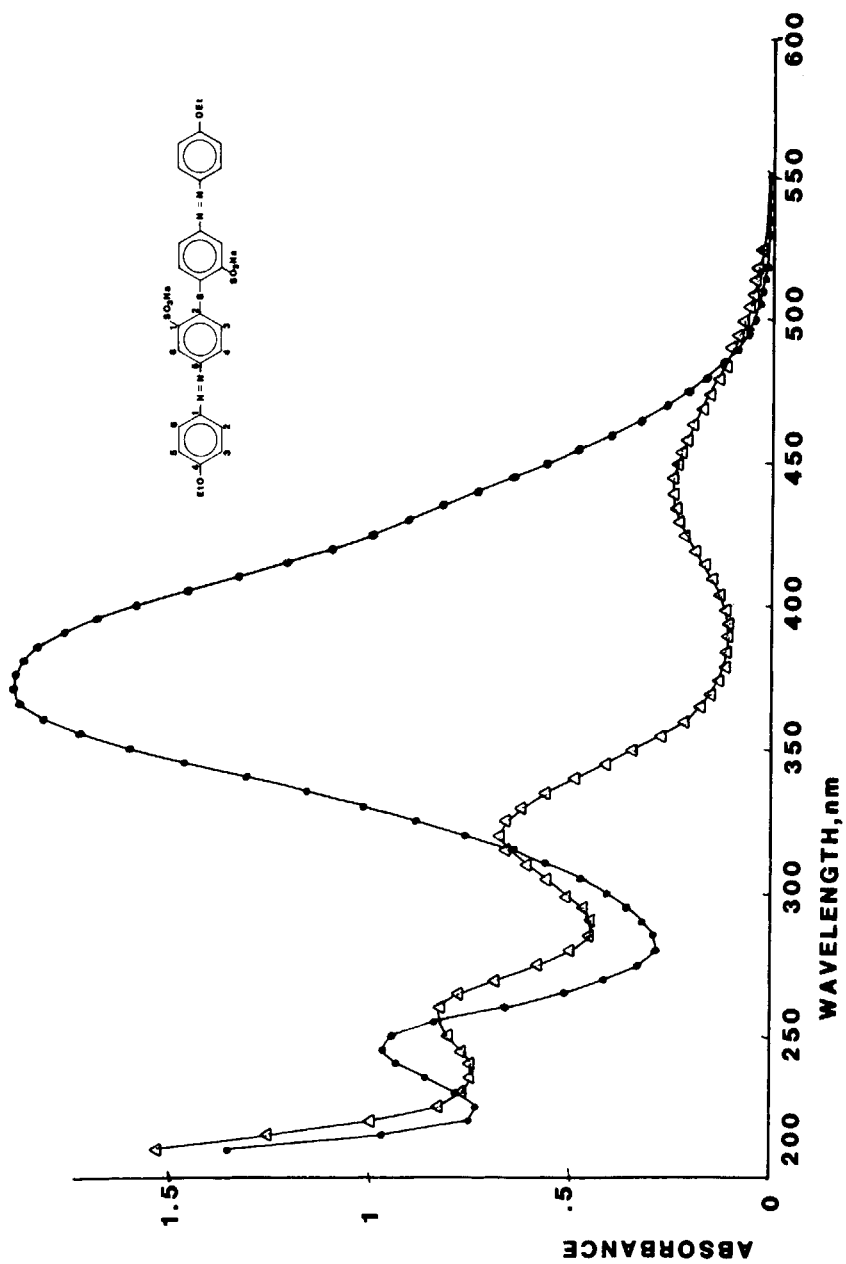


Fig. 3. Electronic spectra of AY38 isomers: (●) measured all-trans; (△) calculated all-cis. Dye concentration  $4.3 \times 10^{-5} M$ .

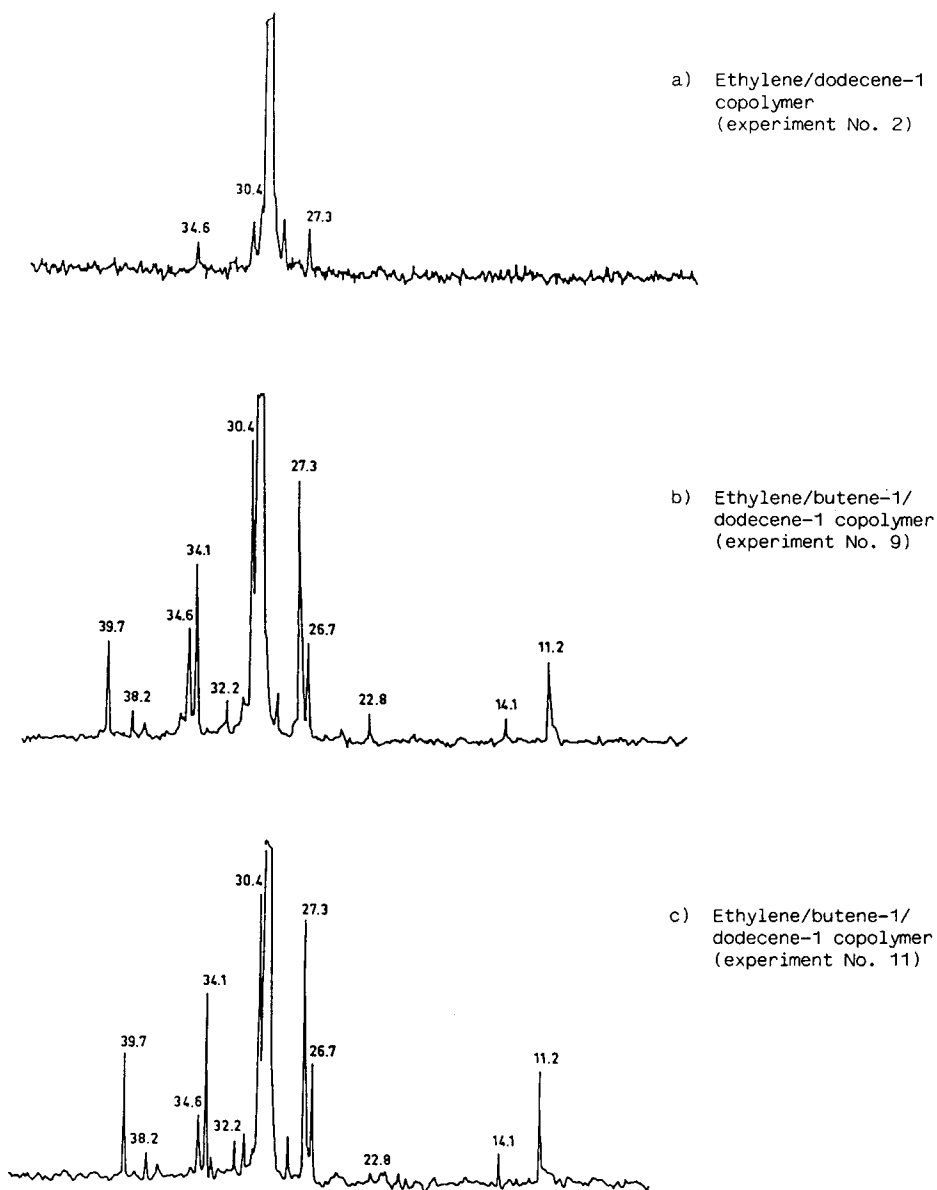


Fig. 1. Typical  $^{13}\text{C}$ -NMR spectra of copolymers. Resonances indicated as ppm TMA. (a) Ethylene/dodecene-1 copolymer (experiment no. 2); (b) Ethylene/butene-1/dodecene-1 copolymer (experiment no. 9); (c) Ethylene/butene-1/dodecene-1 copolymer (experiment no. 11).

detected in the spectra from resonances typical for branches containing more than six carbon atoms at 38.2, 34.6, 32.2, 30.4, 27.3, 22.8, and 14.1 ppm TMS.<sup>2</sup> The DSC curves in Figure 2 show a melting range at about 100°C, the size of which increases with increasing dodecene-1 content. Table II gives the properties of prepared samples. Crystallinity has been reduced remarkably, when the comonomer content in the polymer has been increased. Crystallinities in Figure 3 are presented as a function of dodecene-

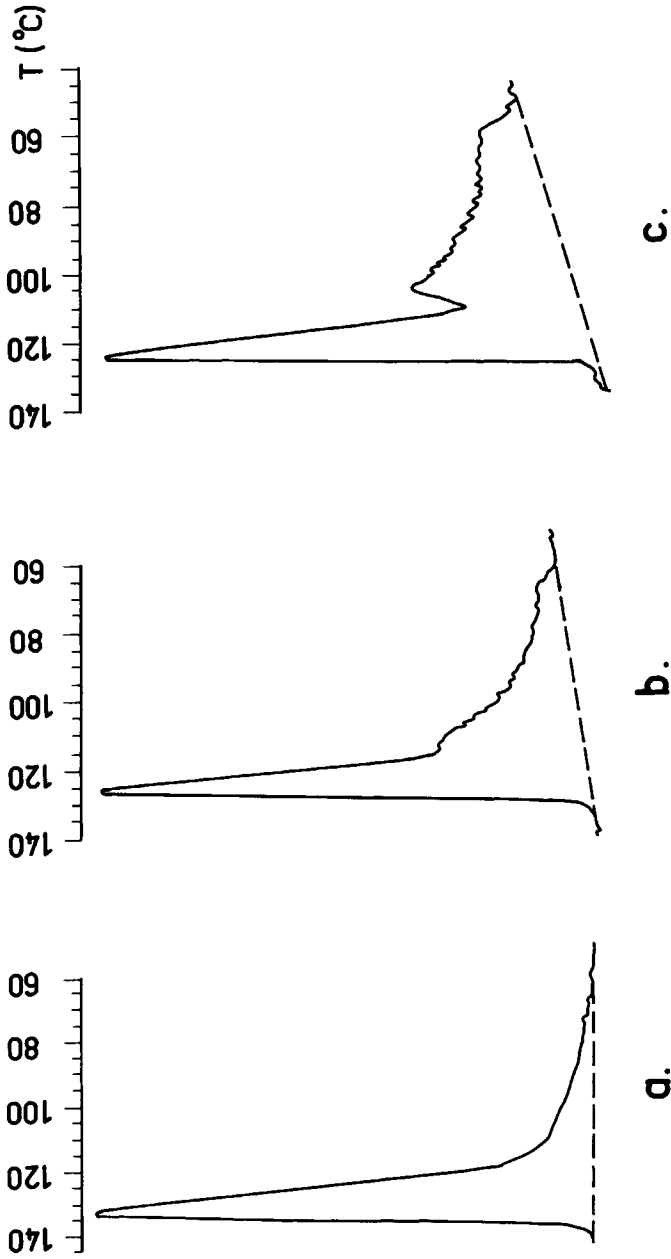


Fig. 2. Typical DSC curves of prepared copolymers. (a) Ethylene/dodecene-1 copolymer (experiment no. 2); (b) Ethylene/butene-1/dodecene-1 copolymer (experiment no. 9); (c) Ethylene/butene-1/dodecene-1 copolymer (experiment no. 11).

TABLE II  
Polymer Composition and Basic Properties

Experiment no.	Polymer composition				$T_m$ (°C)	Crystallinity (%)	Density (g/dm <sup>3</sup> )	$M_v$ 10 <sup>5</sup> g/mol	$\frac{\overline{M}_w}{\overline{M}_n}$
	Ethyl branches/100°C	Butene-1 concn (wt %)	Dodecene-1						
			Branches/100°C	concentration (wt %)					
1	—	—	<0.2	<3	136	67	>944	4.0	6.2
2	—	—	<0.2	<3	132	60	938	3.6	6.3
3	0.2	0.9	0.1-0.3	2-5	130	59	930	1.8	6.5
4	0.4	1.6	0.9	9.6	125	48	926	1.4	8.0
5	1.2	4.6	0.7	7.4	126	46	924	1.5	8.5
6	1.5	5.0	1.0	10	125	44	923	1.2	7.6
7	0.9	3.4	<0.1	<1	127	48	930	1.3	7.7
8	0.8	3.0	<0.2	<3	128	54	930	2.3	10
9	1.4	5.4	0.3	2.8	125	40	922	1.2	6.8
10	2.0	7.0	0.8	8.5	127	38	913	1.3	8.2
11	1.7	6.2	0.7	8.0	125	32	908	1.5	7.9
12	1.6	6.0	1.0	10	124	30	905	1.1	5.7
13	1.5	5.3	1.5	8.0	125	39	915	0.9	7.3
14	1.8	6.7	0.8	8.1	125	35	913	1.2	9.3

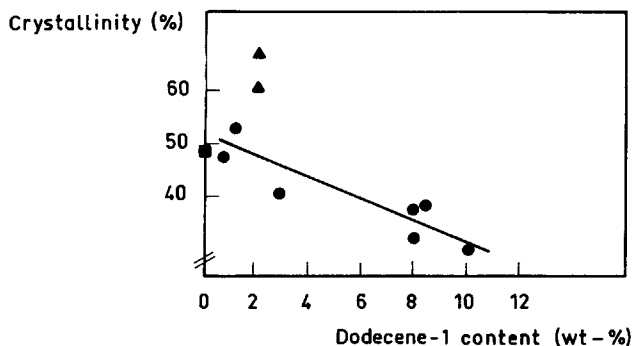


Fig. 3. Effect of dodecene-1 content of copolymers on crystallinity. (●) ethylene/butene-1/dodecene-1 copolymer (butene-1 content 5 wt %); (■) ethylene/butene-1 copolymer (butene-1 content 5 wt %); (▲) ethylene/dodecene-1 copolymer.

1 for samples polymerized at 90°C, and a clear reduction in crystallinity with increasing dodecene-1 content can be seen. When comonomer contents increased, the main melting peak temperature decreased to 124–125°C. Reduction of melting temperature according to density is shown in Figure 4. The lowest densities obtained were 905–910 g/dm<sup>3</sup>. The dependence of density on dodecene-1 content is shown in Figure 5. Crystallinity and density have a clear dependence on each other. According to the DSC curves, measured crystallinity decreased from 50 to 30% when density was lowered from 930 to less than 910 g/dm<sup>3</sup>.

Dodecene-1 produced the same effect as detected in terpolymerizations with decene-1. Dodecene-1 was more reactive when butene-1 was present in the reactor. Experiments were carried out at 80 and 90°C, but the effect of the polymerization temperature was small. It is also clearly seen that dodecene-1 content in the polymer remained at a low level when butene-1 was not present in the reactor. In Figure 6, the effect of initial butene-1 concentration in the reactor to the polymers butene-1 and dodecene-1 contents is shown. Initial dodecene-1 concentration was kept constant at 0.48 mol/dm<sup>3</sup>. Dodecene-1 content in the polymer increased from less than 3

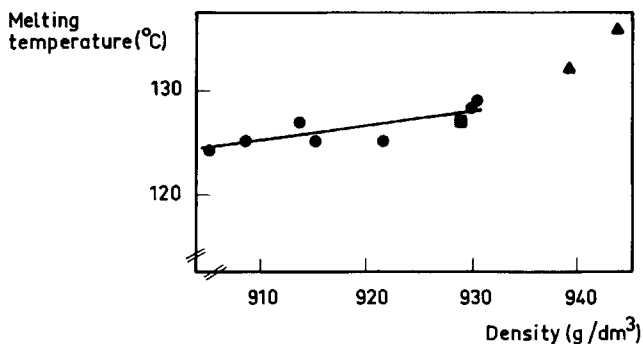


Fig. 4. Dependence of copolymer melting temperature on dodecene-1 content of copolymer. Symbols are explained in Figure 3.

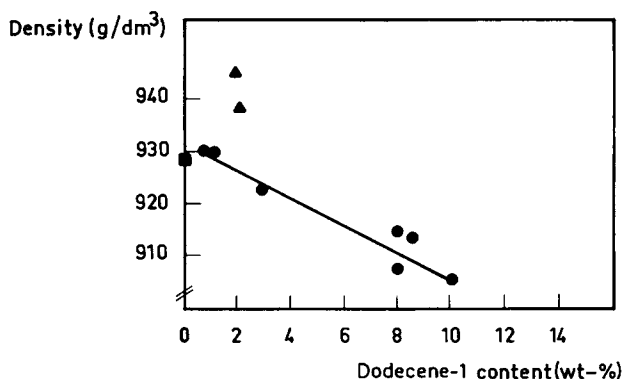


Fig. 5. Dependence of copolymer density on decene-1 content of polymer. Symbols are explained in Figure 3.

wt % to 8–10 wt %, when initial butene-1 concentration changed from zero to over  $0.2 \text{ mol/dm}^3$ . When butene-1 concentration in the reactor was further increased, dodecene-1 concentration stabilized at a constant level. Butene-1 content in the polymer continued to increase in the same way as with ethylene/butene-1 copolymers.

In polymerizations with high butene-1 concentrations in the reactor, the increment in the amorphous polymer was substantial. This was evident in the crystallinities measured by DSC and in the formation of soluble polymer, which caused reactor fouling. The composition of both soluble and insoluble polymer was analyzed from ethylene/butene-1/dodecene-1 terpolymers. The suspension taken out of the reactor after the reaction period was divided into two parts. One part was treated as earlier described.<sup>1</sup> The other part was filtrated without the addition of isopropanol, so that the heptane soluble polymer was obtained in the solution. After filtration it was precipitated by isopropanol. The properties of the fractions are given in Table III.

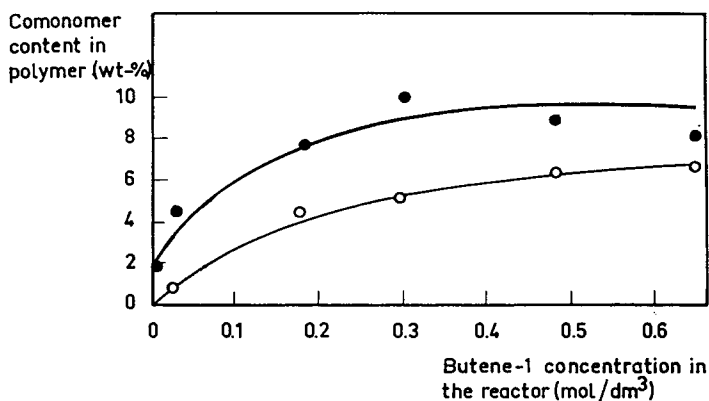


Fig. 6. Effect of initial butene-1 concentration in the reactor on comonomer content measured from the terpolymers. Polymerization temperature was  $90^\circ\text{C}$ , and dodecene-1 concentration in the reactor was  $0.48 \text{ mol/dm}^3$ : (○) butene-1 content; (●) dodecene-1 content.





We can assume that butene-1 causes a sterically less-hindered structure in the growing chain, allowing long  $\alpha$ -olefins to react. Besides, there will be butene-1 comonomer branches along the polymer chain, the amount depending on butene-1 concentration.

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