Copolymerization of Propylene with Butene-1 Catalyzed by Triethylaluminum and Vanadium Trichloride or Vanadyl Trichloride

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Natta et al.[1] have studied the copolymerization of ethylene with propylene by using triethylaluminum and vanadium tetrachloride or vanadyl trichloride; Phillips and Carrick[2] have also synthesized the random copolymer of ethylene and propylene by using a hydrocarbon soluble catalyst, VCl_4-$(C_6H_5)_4Sn$-$AlBr_3$. Junghanns et al.[3] have reported the copolymerization of ethylene with propylene by using alkylaluminum chloride ($AlRCl_2$ or $1/2Al_2R_3Cl_3$) and vanadyl chloride.

Studies of the copolymerization of other olefins were described by Dunham,[4] who examined the effect of side-chain structure on the properties of poly-α-olefin, and by Reding[5] who synthesized the copolymer of 3-methylbutene-1 and 4-methylpentene-1 by using triisobutyl-aluminum and vanadium trichloride. Anderson et al.[6,7] carried out the copolymerization of styrene with 4-methylpentene-1 or 5-methylhexene-1 and determined the monomer reactivity ratio of the monomers. Mark[8] commented on the usefulness of the copolymer of propylene and butene-1.

The present author has been interested in the characterization of the copolymer of propylene and butene-1, whose homopolymers have the same identity period (6.5Å) as the orientated polymers.[9] In the present paper, the copolymerization of propylene with butene-1 by using triethylaluminum combined with vanadium trichloride or vanadyl trichloride will be reported.

Experimental

Polymerization.—A given quantity of vanadium trichloride or vanadyl trichloride and a glass ampoule containing triethylaluminum were charged with *n*-hexane (2—5 cc.) in a stainless steel autoclave. After the autoclave had been flushed with a nitrogen stream, liquid propylene and butene-1 were introduced through a steel pipe into the autoclave cooled to $-78°C$, and the amounts of the monomers were determined by weight. As soon as the glass ampoule in the autoclave had been broken by vigorous shaking, the autoclave was dipped in a thermostatic bath. The polymers obtained were then washed repeatedly by boiling methanolic hydrochloric acid or methanol and dried in a vacuum. As a control, the isotactic polypropylene sample for X-ray diffraction measurement was prepared by the same procedure.

Samples for Infrared Spectrum and X-Ray Diffraction.—The polymer dissolved in toluene or xylene was cast on mercury, and the solvent was gradually evaporated by heating. The films thus obtained were used for infrared spectrum and X-ray diffraction measurements. The optical densities at $970\,cm^{-1}$ were determined according to the base line method.

Intrinsic Viscosity.—The copolymers were fractionated by solvent extraction with a Soxhlet extractor, and the intrinsic viscosity of each fraction was determined in toluene at 100°C.

Results and Discussion

The results of copolymerization with various monomer ratios are listed in Tables I and II. In the propylene-butene-1 copolymer, there are two characteristic bands, at $970\,cm^{-1}$ and $760\,cm^{-1}$, in the infrared spectrum which are independent of the crystallinity of the copolymers. The former band, at $970\,cm^{-1}$, has been attributed to the CH_2 rocking, C–C stretching, CH_3 wagging and rocking modes of polypropylene,[10] while the later band $760\,cm^{-1}$ may be attributed to the CH_2 rocking vibration of the ethyl group of polybutene-1.[11] Therefore the optical density ratio, $D(970\,cm^{-1})/D(760\,cm^{-1})$, may be accepted as a measure of the

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[1] G. Natta et al., *Chim. e Ind. (Milan)*, **39**, 733 (1057); *Chim. e Ind. (Milan)*, **39**, 743 (1957); *Chim. e Ind. (Milan)*, **39**, 825 (1957).

[2] G. W. Phillips and W. L. Carrick, *J. Am. Chem. Soc.*, **84**, 920 (1962).

[3] E. Junghanns, A. Gumboldt and G. Bier, *Makromol. Chem.*, **58**, 18 (1962).

[4] K. R. Dunhanns, J. Vandenberghe, J. W. H. Faber and L. E. Contois, *J. Polymer Sci.*, **A1**, 751 (1963).

[5] F. P. Reding and C. W. McGary, U. S. Pat. 3091601 (1963); *Chem. Abstr.*, **59**, 5282 (1963).

[6] I. H. Anderson, G. M. Burnett and J. T. Tait, *Proc. Chem. Soc.*, **1960**, 225.

[7] I. H. Anderson, G. M. Burnett and J. T. Tait, *J. Polymer Sci.*, **56**, 391 (1962).

[8] H. Mark, Presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

[9] G. Natta, *Makromol. Chem.*, **35**, 94 (1960). For isotactic polybutene-1, the identity period was reported to be 6.85 Å in *Makromol. Chem.*, **21**, 240 (1956).

[10] C. Y. Liang and F. G. Pearson, *J. Mol. Spectroscopy*, **5**, 290 (1960).

[11] M. C. Harvey and A. D. Ketley, *J. Appl. Polym. Sci.*, **5**, 247 (1961).

Table I. Copolymerization of propylene with butene-1 catalyzed by triethylaluminum and vanadium trichloride[a]

$(\text{AlEt}_3)=8.6\times10^{-3}$ mol., $(\text{VCl}_3)=1.27\times10^{-3}$ mol.

Exp. No.	Monomer 10^{-1} mol.		$\frac{\text{Propylene}}{\text{Butene-1}}$ molar ratio	Reaction time, hr.	Conversion %	Optical density ratio[b] $\frac{D(970\ \text{cm}^{-1})}{D(760\ \text{cm}^{-1})}$
1	Butene-1	3.35	0	3.5	24.9	—
2	Butene-1	2.30				
	Propylene	1.21	0.53	3.0	37.1	1.38
3	Butene-1	1.45				
	Propylene	2.21	1.54	2.5	43.0	1.87
4	Butene-1	1.30				
	Propylene	2.20	1.70	4.0	42.5	3.4
5	Butene-1	1.23				
	Propylene	2.50	2.1	2.5	62.1	2.55
6	Butene-1	0.08				
	Propylene	0.285	3.65	2.0	27.3	4.15
7	Butene-1	0.033				
	Propylene	0.338	10.4	2.5	38.7	7.8

a) All polymerizations were carried out in a thermostat at 60°C.

b) All samples for optical density measurements were unfractionated. The artificial mixture of polypropylene (30 wt.%) and polybutene-1 (70 wt.%) showed the optical density ratio, $D(974\ \text{cm}^{-1})/D(760\ \text{cm}^{-1})$, of 0.86.

Table II. Copolymerization of propylene with butene-1 catalyzed by triethylaluminum and vanadyl trichloride[a]

$(\text{AlEt}_3)=8.6\times10^{3}$ mol., $(\text{VOCl}_3)=3.46\times10^{-3}$ mol.

Exp. No.	Monomer 10^{-1} mol.		$\frac{\text{Propylene}}{\text{Butene-1}}$ molar ratio	Reaction time, hr.	Conversion %	Optical density ratio[b] $\frac{D(970\ \text{cm}^{-1})}{D(760\ \text{cm}^{-1})}$
8	Butene-1	3.29	0	2.0	48.1	—
9	Butene-1	1.81				
	Propylene	1.26	0.715	2.0	41.5	0.86
10	Butene-1	1.58				
	Propylene	2.38	1.51	2.0	46.0	1.74
11	Butene-1	1.02				
	Propylene	2.99	3.0	2.0	60.5	4.0
12	Butene-1	0.8				
	Propylene	3.26	5.9	2.0	72.1	15.0

a) All polymerizations were carried out at 30°C.

b) All samples for optical density measurements were not fractionated.

polypropylene content of the copolymers. The infrared spectra of the typical unfractionated copolymers obtained by using triethylaluminum combined with vanadium trichloride or vanadyl trichloride catalysts are shown in Fig. 1.

According to Luongo[12] and Nishioka et al.[13], the determination of the isotactisity of polypropylene and polybutene-1 can be made by the measurement of the optical density ratios, $D(995\ \text{cm}^{-1})/D(974\ \text{cm}^{-})$ and $D(917\ \text{cm}^{-1})/D(1148\ \text{cm}^{-1})$ respectively. Both the isotactic sensitive band at 917 cm^{-1} from the butene-1 unit sequence and that at 995 cm^{-1} from the propylene unit sequence are inclined to weaken in the spectra of copolymers obtained by using triethylaluminum and vanadium trichloride catalysts, as may be seen in Fig. 1 (spectrum II). This suggests that a new crystalline copolymer is formed by using the above catalyst, a theory supported by the X-ray diffraction patterns shown in Fig. 2 and Table IV. In the copolymers from triethylaluminum and vanadyl trichloride catalysts, the isotactic-sensitive bands from the butene-1 unit and propylene unit sequences are recognized to be much weakened in optical density. Therefore, these copolymers have scarcely any of the isotactic chains of either monomer unit sequence;

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[12] J. P. Luongo, *J. Appl. Polym. Sci.*, 3, 302 (1960).

[13] A. Nishioka, K. Yanagisawa and T. Naraba, Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

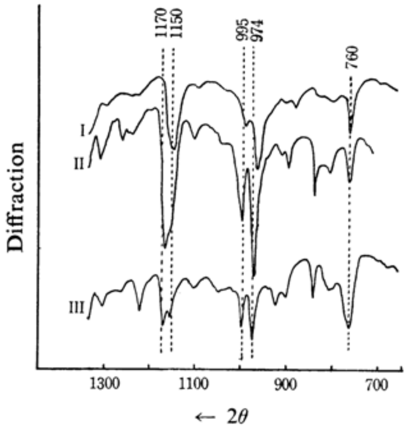

Fig. 1. Comparison of infrared spectra of copolymer and mixed polymer.
I: Copolymer from triethylaluminum and vanadyl trichloride (No. 10)
II: Copolymer from triethylaluminum and vanadium trichloride (No. 4)
III: Mixed polymer (polybutene-1/polypropylene=7/3)

moreover, they are found to be new amorphous copolymers by the X-ray diffraction mearurements. The infrared absorption spectra of the copolymers and mixed homopolymers are compared in Fig. 1. Copolymers lack the absorption at 1170 cm^{-1}, whereas the mixed homopolymers show two absorptions, at 1150 cm^{-1} and 1170 cm^{-1}, which are due to the component homopolymers. It may be noted also that the copolymers show an absorption at 970 cm^{-1} instead of that at 974 cm^{-1} which is due to the isotactic polypropylene. Consequently, it is clear that the polymers here obtained are not mixtures of polypropylene and polybutene-1 but are copolymers.

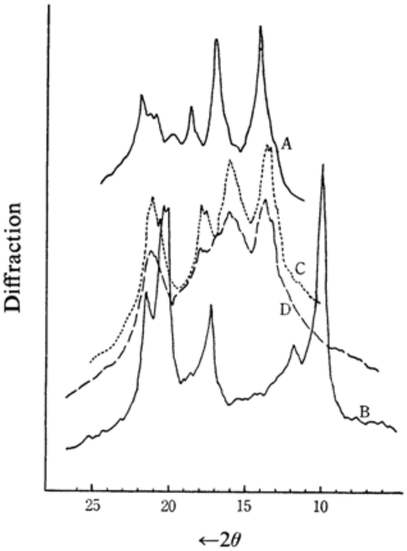

Fig. 2. X-Ray diffraction patterns of polypropylene, polybutene-1 and copolymer obtained by using triethylaluminum and vanadium trichloride catalyst
A: Isotactic polypropylene
B: Polybutene-1 (No. 1)
C: Unfractionated propylene-butene-1 copolymer (No. 3)
D: *n*-Hexane extractable propylene-butene-1 copolymer (No. 3)

The copolymers were fractionated by solvent extraction (diethyl ether, *n*-hexane, isooctane) into four portions, as is shown in Table III. It was found, from the spectrum change between 1150 cm^{-1} and 1170 cm^{-1}, that the portion extracted by a lower boiling solvent (diethyl ether) showed the absorption at 1150

TABLE III. THE FRACTIONATIONS AND INTRINSIC VISCOSITIES OF COPOLYMERS[a)]

No.	Used catalysts	Propylene/Butene-1 molar ratio	Solvent extractions							
			Et_2O wt.%	[η]	*n*-hex. wt.%	[η]	iso oct. wt.%	[η]	residue wt.%	[η]
9	$AlEt_3$, $VOCl_3$	0.715	77.4	0.22	12.9	0.51	8.1	2.25	1.6	—
11	$AlEt_3$, $VOCl_3$	3.0	52.0	0.31	12.2	0.95	6.3	2.1	29.5	2.5
3	$AlEl_3$, VCl_3	1.54	47.5	0.82	18.0	1.8	9.8	3.8	24.7	2.1

a) The intrinsic viscosities were measured in toluene at 100°C.

TABLE IV. d-SPACING OF COPOLYMER AND HOMOPOLYMER

Isotactic polypropylene		Polypropylene ($AlEt_3$, $VOCl_3$)		Polybutene-1 ($AlEt_3$, VCl_3)		Polybutene-1 ($AlEt_3$, $VOCl_3$)		Copolymer (No. 6) ($AlEt_3$, VCl_3)	
2θ	*d*	2θ	*d*	2θ	*d*	2θ	*d*	2θ	*d*
14.3	6.17	14.3	6.17	10.0	8.84	10.0	8.84	13.8	7.19
17.1	5.48	17.0	5.48	11.8	8.64	17.4	5.47	16.2	5.52
18.7	4.90	18.7	4.90	17.4	5.47	20.4	4.42	18.0	4.93
21.4	4.38	21.3		20.4	4.42	21.4	4.38	21.3	4.39
21.6		21.7		21.4	4.38				
22.2									

cm^{-1} of polybutene-1. On the other hand, that extracted by a higher boiling solvent (isooctane) showed the absorption at 1167 cm^{-1}, which was near to that at 1168 cm^{-1} ascribed to polypropylene. The polymer extracted by *n*-hexane had the absorption in the middle, between 1168 cm^{-1} and 1150 cm^{-1}. It was also ascertained that the polymer extracted by a lower boiling solvent was richer in the butene-1 unit sequence, while that extracted by a higher boiling solvent was richer in the propylene unit sequence. The optical density ratio, $D(970\text{ cm}^{-1})/D(760\text{ cm}^{-1})$ was lower for the portion extracted by a lower boiling solvent than for that extracted by a higher boiling solvent.

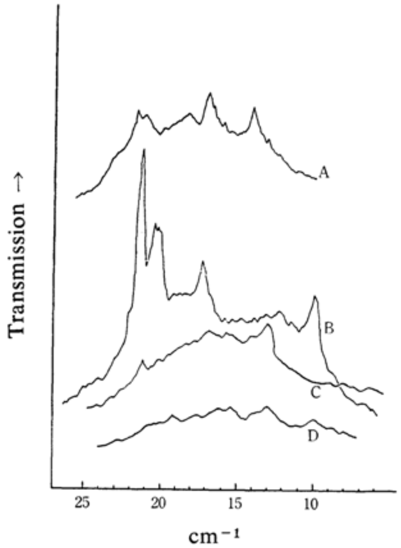

Fig. 3. X-ray diffraction patterns of polypropylene, polybutene-1 and copolymer obtained by using triethylaluminum and vanadyl trichloride catalyst

A: Polypropylene
B: Polybutene-1 (No. 8)
C: Unfractionated propylene-butene-1 copolymer (No. 10)
D: *n*-Hexane extractable propylene-butene-1 copolymer (No. 9)

It was found that the copolymers obtained from propylene and butene-1 had different X-ray diffractions from those of the homopolymers. The copolymer obtained by using triethylaluminum and vanadium trichloride is crystalline; the d-spacing is indicated in Table IV together with that of homopolymers. The X-ray diffraction patterns of crystalline copolymers are shown in Fig. 2. The copolymer prepared with the triethylaluminum-vanadyl trichloride catalyst was amorphous; the X-ray diffraction patterns are shown in Fig. 3.

From the infrared spectra and X-ray diffraction of the copolymers, may it be concluded that the triethylaluminum-vanadium trichloride catalytic system is a stereospecific one, one which produces the crystalline copolymers in the copolymerization of propylene with butene-1, while, on the other hand, the triethylaluminum-vanadyl trichloride catalytic system is a less stereospecific one, one which produces the amorphous copolymers in the copolymerization of the same monomers.

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