

# Radical Copolymerization of Ethylene and 2-Phenyl-3-Vinyloxirane

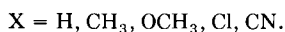
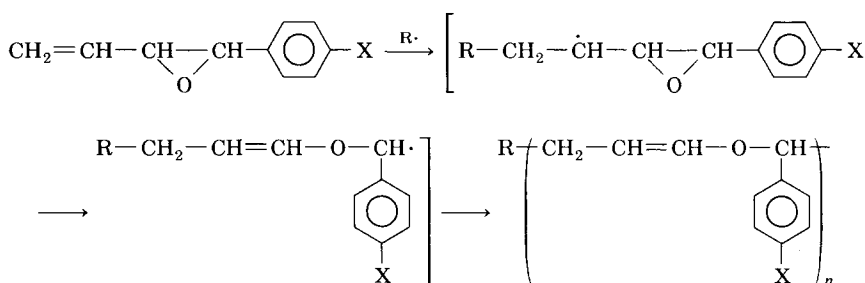
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## Synopsis

The radical copolymerization of ethylene and 2-phenyl-3-vinyloxirane was carried out under high pressure to obtain the corresponding copolymers. The structure of the obtained copolymers was discussed by the data of infrared and nuclear magnetic resonance.

## INTRODUCTION

A large number of studies on the copolymerization of ethylene with a wide variety of vinyl monomer, to modify polyethylene, have been reported. It has been reported that the monomers as spiro-dixylylene,<sup>1</sup> vinylcyclopropanes,<sup>2</sup> unsaturated spiro orthocarbonates,<sup>3</sup> and cyclic ketene acetals such as 2-methylene-1,3-dioxepane and 2-methylene-4-phenyl-1,3-dioxolane<sup>4</sup> undertake the ring-opening isomeric polymerization. These monomers are expected to undergo the copolymerization with various vinyl monomers to incorporate the functional groups such as ester and carbonate into the polymers. Recently, the radical ring-opening polymerization of 2-phenyl-3-vinyloxirane derivatives has been reported.<sup>5,6</sup>



In this article, we wish to report the radical copolymerization of ethylene and 2-phenyl-3-vinyloxirane (PVO) under high pressure with a view to modify polyethylene chemically and clarify the structure of the obtained copolymers.

## EXPERIMENTAL

PVO was synthesized from allyldimethylsulfonium salt and benzaldehyde, according to modified procedure of Hatch.<sup>7</sup> The purity of ethylene used was 99.98% and its oxygen content was less than 1 ppm.

Copolymerization of ethylene and PVO were carried out batchwise with organic peroxides as initiators at 900 kg/cm<sup>2</sup> and 120–155°C in an autoclave. The autoclave equipped with an agitator and cooling coil to remove polymerization heat was specially designed for high pressure polymerization of ethylene.

The autoclave was purged with nitrogen and ethylene and was controlled at desired temperature. The compressed ethylene was charged into the autoclave, then PVO and the initiator were pumped through the inlet line using 50 mL of benzene/*n*-hexane (30 : 20 vol) mixture as a carrier solvent.

The obtained polymers were dissolved into hot toluene. Then the polymers were isolated by pouring the solution into stirred methanol. This treatment was carried out twice. The polymers thus obtained were dried under reduced pressure.

## RESULTS AND DISCUSSION

The results of the copolymerizations are summarized in Table I. The obtained polymers were white powder and completely soluble in hot toluene except for No. 4 polymer which was pale yellow powder.

The infrared (IR) spectra of ethylene-PVO copolymer and PVO homopolymer (poly PVO) are shown in Figure 1.

In the spectrum of the copolymer, the absorption bands of  $(-\text{CH}_2-)_n$  (1465, 2930, 720, 730 cm<sup>-1</sup>), ether linkage (1100–1200 cm<sup>-1</sup>), and aromatic ring (1603 cm<sup>-1</sup>) were observed. But the absorption at 1662 cm<sup>-1</sup> due to C=C bond of C=C—O—C group, which was intensely observed in the spectrum of poly PVO, was decreased. Moreover, the absorption of carbonyl group (1720 cm<sup>-1</sup>) was observed.

TABLE I  
Copolymerization of Ethylene and PVO<sup>a</sup>

No.	PVO/ethylene + PVO (mol%)	Temp. (°C)	Initiator	(mol%)	Yield <sup>b</sup> (%)	PVO Cont. <sup>b,c</sup> (mol%)	[ $\eta$ ] <sup>b,d</sup>
1	0.82	120	DTBP	0.046	17	0.89	0.39
2	0.82	135	DTBP	0.046	15	0.92	0.39
3	1.57	135	DCP	0.12	19	1.7	0.23
4	3.36	135	DTBP	0.37	22	3.0	—
5	0.86	155	MHP <sup>e</sup>	0.072	6	1.1	0.46

<sup>a</sup> Polymerization; 900 kg/cm<sup>2</sup>, 4.5 h.

<sup>b</sup> Insoluble part in MeOH.

<sup>c</sup> Estimated by intensity of the aromatic ring carbon signal of <sup>13</sup>C-NMR spectra.

<sup>d</sup> 40 mg/20 mL-Decalin, at 135°C.

<sup>e</sup>  $\text{CH}_3-\text{C}(\text{H})-\text{C}(\text{CH}_3)_2-\text{O}-\text{O}-\text{H}$ .

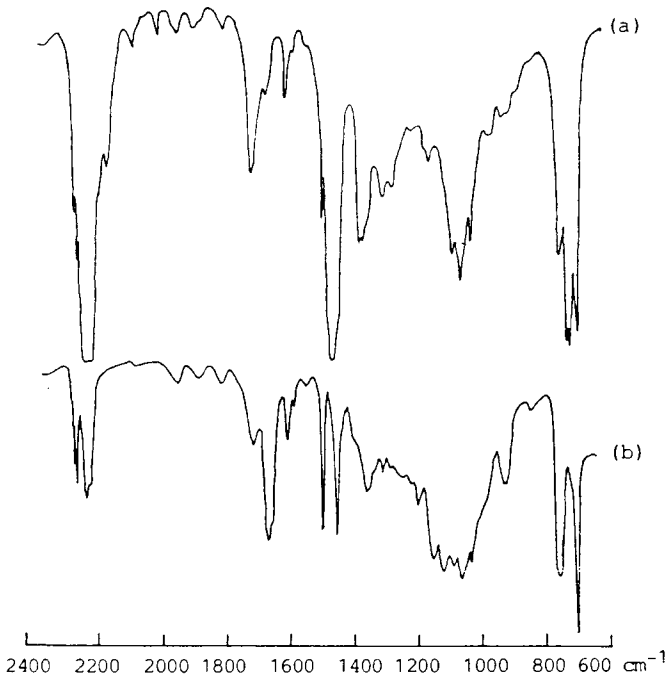


Fig. 1. IR spectra of ethylene-PVO copolymer (a) and poly PVO (b). (a) Obtained by No. 3 in Table I. (b) Obtained by polymerization in a sealed tube.

TABLE II  
<sup>13</sup>C-NMR Data of the Polymers

Polymer	Structure	Chemical shift (ppm)
Ethylene-PVO	$\text{-(CH}_2\text{)}_n\text{-CH-O-CH-}$	29.8
Copolymer <sup>a</sup>		80.5, 83.0, 144.1
Poly PVO <sup>b</sup>		A: 32.7, 36.4 B: 102.1 C, E: 141.3-147.1 D: 80.2-85.2 F-H: 126.1-128.6

<sup>a</sup>Copolymer obtained by No. 3 in Table I, in ODCB at 110°C.

<sup>b</sup>Polymer obtained by polymerization in a sealed tube, in CDCl<sub>3</sub> at 25°C.

TABLE III  
<sup>1</sup>H-NMR Data (ODCB, 110°C) of Ethylene-PVO Copolymer<sup>a</sup>

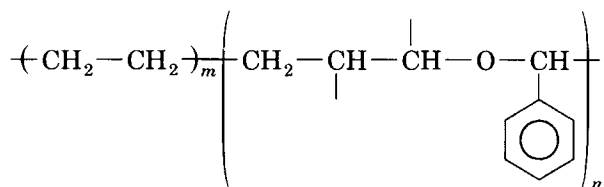
Structure	Chemical shift (ppm)
$\begin{array}{c} \text{-(CH}_2\text{)}_n\text{-} \\   \\ \text{-CH-O-CH-} \\   \quad   \\ \quad \text{C}_6\text{H}_5 \end{array}$	1.28
$\begin{array}{c} \text{C}_6\text{H}_5 \end{array}$	3.88, 4.72

<sup>a</sup> Obtained by No. 3 in Table I.

<sup>13</sup>C nuclear magnetic resonance (NMR) spectra of ethylene-PVO copolymer and poly PVO are summarized in Table II. The signals characteristic of C=C—O—C group were not observed in the spectrum of the copolymer, which was consistent with the results of IR spectroscopy. But the existence of carbonyl group was not confirmed. These facts are considered to be due to low content of carbonyl group in the polymer and low sensitivity of its <sup>13</sup>C-NMR signal.

<sup>1</sup>H-NMR spectrum of the copolymer is indicated in Table III. The signals due to C=C—O—C group, which were observed in the spectrum of poly PVO,<sup>5</sup> were not found.

The results of these IR and NMR spectroscopy suggest that ethylene-PVO copolymer consists mainly of the structure shown in the following formula:



and that it also contains small amount of carbonyl group.

TABLE IV  
 IR Data of the Polymer Obtained by Polymerization  
 of Ethylene in the Presence of Poly PVO<sup>a,b</sup>

Structure	Absorption band (cm <sup>-1</sup> )
$\begin{array}{c} \text{-(CH}_2\text{)}_n\text{-} \\ \text{C-O-C} \end{array}$	720, 730, 1465, 2930 1000-1200
	1600
C=O	1720

<sup>a</sup> Polymerization : 900 kg/cm<sup>2</sup>, 135°C, 4.5 h, initiator DTBP, ethylene 1450 g, poly PVO 4.0 g.

<sup>b</sup> Cold toluene-insoluble part.



Homopolymerization of PVO was carried out under compressed nitrogen at a pressure of 900 kg/cm<sup>2</sup> and 135°C. It was confirmed by IR spectroscopy that the structure of the resultant polymer was the same as that of poly PVO obtained in a sealed tube. This result might suggest the pressure had no influence on the structure of the polymer.

Polymerization of ethylene was carried out in the presence of poly PVO at 900 kg/cm<sup>2</sup> and 135°C. The IR spectrum of the cold toluene-insoluble part of the obtained polymer is summarized in Table IV. In this spectrum, the absorption bands due to ether linkage and carbonyl group besides  $(\text{CH}_2)_n$  were observed, but C=C—O—C absorption disappeared completely. Accordingly, it is considered that polyethylene radicals attack C=C bond of poly PVO to obtain a grafted polymer.

From the above-mentioned results, the radical copolymerization of ethylene and PVO is considered to proceed as the Polymerization Scheme.<sup>3</sup>

### References

1. L. A. Errede, *J. Polym. Sci.*, **49**, 253 (1961).
2. I. Cho and K. D. Ahn, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 3169 (1979).
3. T. Endo and W. J. Bailey, *J. Polym. Sci. Polym. Lett. Ed.*, **13**, 2525 (1975).
4. I. Cho and S. Gong, *J. Polym. Sci. Polym. Lett. Ed.*, **20**, 361 (1982); W. J. Bailey, S-R. Wu, and Z. Ni, *Makromol. Chem.*, **183**, 1913 (1982).
5. I. Cho and J-B. Kim, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 433 (1983).
6. T. Endo and N. Kanda, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 1931 (1985).
7. M. J. Hatch, *J. Org. Chem.*, **34**, 2133 (1969).

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