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Copolymerization of *N*-Phenylethylenimine and β-Propiolactone

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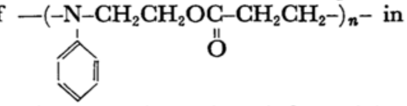
The copolymerization of *N*-phenylethylenimine and β-propiolactone was carried out at 0°C in an acetonitrile solution. *N*-Phenylethylenimine and β-propiolactone copolymerized without any catalyst to give a powdery or a resinous polymer. From the results of a study of the infrared spectrum, X-ray diffraction, differential thermal analysis, and hydrolyses of the copolymer, it was concluded that the homopolymerization of neither monomer took place, and that the copolymer contained the ester structure of  $—(-N-CH_2CH_2O\underset{\overset{\|}{O}}{C}-CH_2CH_2-)_n-$ in the main chain. The monomer reactivity ratios of *N*-phenylethylenimine (r_1) and β-propiolactone (r_2) were estimated to be $r_1=7.5$ and $r_2=0.15$.

It is well known that aziridines polymerize to polyimines[1] with various cationic catalysts, and that β-propiolactone to the crystalline polyester with pyridine or other amines.[2,3] It has already been reported by the present authors[4] that ethylenimine and β-propiolactone serve as mutual polymerization catalysts, and that, when these two substances are mixed in bulk, the copolymerization takes place explosively and gives a polymer mainly with a branching structure of β-propiolactone to the polyethylenimine.

As a part of the investigation of the copolymerization of aziridines and cyclic ester, the copolymerization of *N*-phenylethylenimine and β-propiolactone was studied. It was found that the copolymerization took place without any catalyst and gave a white crystalline copolymer. The purpose of the present paper is to determine the structure and composition of the copolymer by means of a study of the infrared spectrum, X-ray diffraction, the differential thermal analysis, and an analytical study of the hydrolysis products of the copolymer.

Experimental

Copolymerization Procedure. Commercial β-propiolactone was distilled over calcium hydride under reduced pressure at 59°C/20 mmHg. The *N*-phenylethylenimine was prepared according to the literature[5] from β-bromoethylaniline hydrobromide. It was dried over sodium sulfate and fractionated twice before use; bp 70—70.5°C/13 mmHg. The acetonitrile was purified by the usual method.[6]

Measured amounts of β-propiolactone and a solvent were placed into a glass ampule under a nitrogen atmosphere, and then *N*-phenylethylenimine was added to this system at −78°C. After the ampule had been sealed and maintained at 0—1°C for a definite period of time, the products were washed with chloroform and diethyl ether, separated by a centrifuge, and dried *in vacuo*.

Physical Analyses of the Copolymer. The melting point of the copolymer was measured visually in a nitrogen atmosphere in a capillary on an electric heater. The reduced viscosity of a 0.25% solution of 90% formic acid was measured at 35°C with an Ostwald viscometer. The infrared spectrum was obtained with the use of the potassium bromide-pellet technique on a Shimadzu infrared spectrophotometer, Model IR-27. The X-ray diffraction diagram was recorded with a powder camera on a Shimadzu X-ray diffractometer, Model GX-3B. The differential thermogram was obtained with the use of a Rigaku Denki differential thermal apparatus, Model VIP-32.

Determination of the Composition of the Copolymer. The absorption peak of the infrared spectrum at 1740 cm^{-1} assigned to the ester group of β-propiolactone, and that at 1600 cm^{-1} assigned to the phenyl group of *N*-phenylethylenimine were used in order to determine the composition of the copolymer.

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[1] G. D. Jones, in P. H. Plesch, ed., "The Chemistry of Cationic Polymerization," Pergamon, Oxford (1963), Chapter 14.

[2] T. Kagiya, T. Sano and K. Fukui, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 951 (1964).

[3] Y. Etienne and R. Sonlas, *J. Polymer Sci.*, **C4**, 1061 (1964).

[4] T. Kagiya S. Narisawa, K. Manabe, and K. Fukui, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 1741 (1965); T. Kagiya, S. Narisawa, K. Manabe and K. Fukui, *J. Polymer Sci.*, **B3**, 617 (1965).

[5] H. W. Heine, B. L. Kapur and C. S. Mitch, *J. Am. Chem. Soc.*, **76**, 1173 (1954).

[6] A. Weissberger *et al.*, "Technique of Organic Chemistry, Vol VII, Organci Solvents," Interscience Publishers, Inc., New York (1955).

TABLE 1. CORRELATION BETWEEN COMPOSITION OF THE COPOLYMER AND THE OPTICAL DENSITY RATIO, D_{1740}/D_{1600}

Sample No.	Elementary analyses			Composition of copolymer (mol%)		Optical density ratio D_{1740}/D_{1600}
	C	H	N	Imine	Lactone	
1	77.81	7.59	11.17	97.0	3.0	0.215
2	77.21	7.78	10.99	94.0	6.0	0.289
3	69.73	6.94	9.69	88.4	11.6	0.369
4	75.47	7.19	9.86	76.1	23.9	0.688
5	70.11	7.07	9.11	75.5	24.5	0.517
6	66.06	6.57	8.35	71.0	29.0	0.690
7	65.81	6.49	8.23	69.4	30.6	0.883
8	73.20	7.13	9.17	68.2	32.8	1.04
9	73.80	6.81	9.05	66.9	33.1	0.906

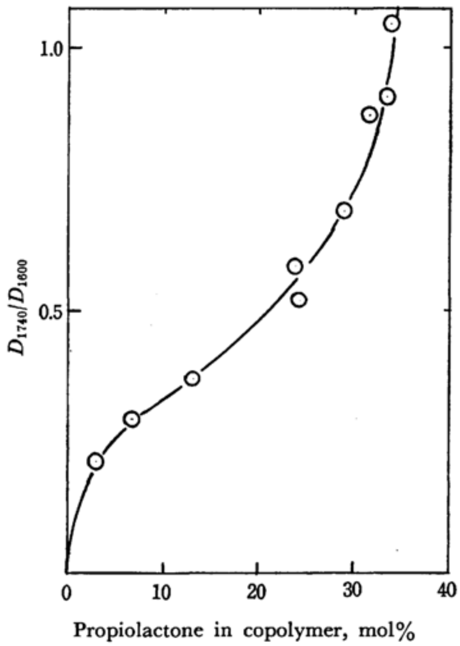


Fig. 1. Calibration curve of the copolymer of *N*-phenylethylenimine and β-propiolactone.

The calibration curve was obtained by plotting the optical density ratio, D_{1740}/D_{1600}, against the mole fraction of β-propiolactone, which was itself determined from the carbon and nitrogen contents by elementary analyses (Fig. 1 and Table 1).

Polymers of *N*-Phenylethylenimine and β-Propiolactone. A white crystalline polymer (mp 287—292°C) of *N*-phenylethylenimine was obtained by polymerization in water at 0°C without a catalyst, while the polymerization of β-propiolactone was carried out in acetonitrile at 0°C with a pyridine catalyst.

Hydrolysis of the Copolymer. In 5 m*l* of 1/10 N sodium hydroxide-ethanol, about 70 mg of the copolymer were hydrolyzed under reflux for 20 hr and then back-titrated with 1/20 N hydrochloric acid, using a 5% alcoholic solution of phenolphthalein as an indicator.

Reaction of Poly-*N*-phenylethylenimine with β-Propiolactone. A mixture of 0.293 g of poly-*N*-phenylethylenimine, 0.571 g of β-propiolactone, and 5 m*l* of acetonitrile was heated in a sealed tube at 35°C for 20 hr without a catalyst, the reaction product was then washed in chloroform and dried *in vacuo*. The amounts of carboxylic acid in these polymers were determined as follows. About a 70-mg portion of the polymer was added to 5 m*l* of 1/10 N sodium hydroxide-ethanol, and the solution was back-titrated with 1/20 N hydrochloric acid.

Results and Disscusion

The results of the copolymerization without a catalyst in acetonitrile at 0°C are summarized in Table 2. The copolymer obtained was a white powdery or a yellowish resinous solid polymer which was soluble in formic acid, but insoluble in chloroform, ethanol, dimethylformamide, and other organic solvents. The melting points of the copolymers were 245°C to 279°C, between those of poly-β-propiolactone (75°C) and poly-*N*-phenylethylenimine (287—292°C).

The infrared spectra of the resulting polymer showed the characteristic absorptions at 1740 cm^{-1} and 1600 cm^{-1} based on the ester linkage (β-propiolactone unit) and the benzene nucleus (*N*-phenylethylenimine unit) respectively (see Fig. 2). In order to determine whether the polymer obtained here was the copolymer or a mixture of the corresponding homopolymers, the resulting polymer was fractionated in chloroform, which is a solvent for only poly-β-propiolactone. The infrared spectrum of the fraction insoluble in chloroform is shown in Fig. 2. This infrared spectrum proves that the insoluble fraction of the resulting copolymer contained the β-propiolactone units. On the other hand, the infrared spectrum of the insoluble fraction of the mixture of the homopolymers does not show the peak of the ester linkage. These results indicate that the copolymer of *N*-phenylethylenimine with β-propiolactone was produced.

TABLE 2. COPOLYMERIZATION OF *N*-PHENYLETHYLENIMINE AND β-PROPIOLACTONE WITHOUT CATALYST IN ACETONITRILE AT 0°C

Exp. No.	Monomer (mol)		Time hr	Yield %	$\eta_{sp/c}$ d*l*/g	Melting point °C	Copolymer, mol%	
	N-Phenyl-ethylenimine	β-Propio-lactone					*N*-Phenyl-ethylenimine	β-Propio-lactone
1	0.002	0.018	6.5	8.43	1.26	245—260	67.1	32.9
2	0.004	0.016	2.0	3.43	0.954	259—260	76.2	23.8
3	0.006	0.014	2.0	3.76	1.17	260—263	80.0	20.0
4	0.008	0.012	2.0	3.62	0.980	269—272	85.0	15.0
5	0.010	0.010	2.0	3.71	0.744	275—276	93.2	6.8
6	0.012	0.008	2.0	3.34	0.674	286—287	95.0	5.0
7	0.014	0.006	3.0	3.98	0.523	276—278	95.2	4.8
8	0.016	0.004	6.5	6.85	0.824	275—279	96.6	3.4

Solvent: 10 m*l*

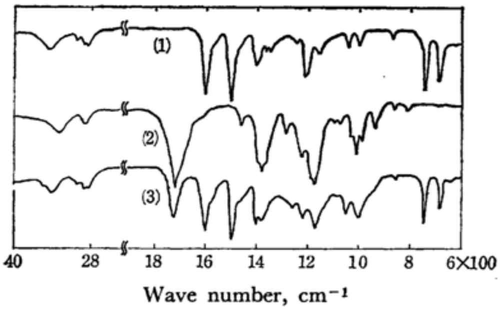


Fig. 2. Infrared spectra of the poly-*N*-phenylethylenimine, poly-β-propiolactone and the copolymer of *N*-phenylethylenimine and β-propiolactone.
(1) Poly-*N*-phenylethylenimine (2) Poly-β-propiolactone (3) Copolymer of *N*-phenylethylenimine and β-propiolactone.

Structure of the Copolymer. X-Ray diffraction diagrams of the copolymer (β-propiolactone 31.8 mol%), the poly-β-propiolactone, and poly-*N*-phenylethylenimine are shown in Fig. 3. The characteristic peaks (2θ) of these polymers are listed in Table 3.

The peaks of the copolymer were similar to characteristic peaks of poly-*N*-phenylethylenimine, but not to those of poly-β-propiolactone. Although no attempt was made to determine the ratio of the crystallinity, it may be considered in view of the relative half-value widths, that the crystallinity of the copolymer is smaller than that of poly-*N*-phenylethylenimine. Figure 4 shows the differential thermogram of the copolymer (β-propiolactone 31.8 mol%) in comparison with those of both homopolymers. We observed the endothermic peak corresponding to the melting point of neither homopolymer, but a new peak of the copolymer was observed, as Fig. 4 shows.

From these results, it may be concluded that neither poly-β-propiolactone nor poly-*N*-phenylethylenimine is present in the copolymer.

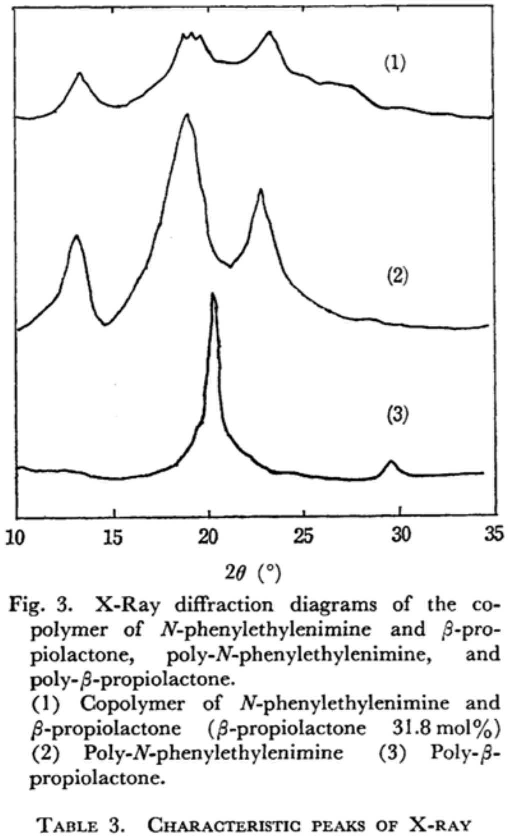


Fig. 3. X-Ray diffraction diagrams of the copolymer of *N*-phenylethylenimine and β-propiolactone, poly-*N*-phenylethylenimine, and poly-β-propiolactone.
(1) Copolymer of *N*-phenylethylenimine and β-propiolactone (β-propiolactone 31.8 mol%) (2) Poly-*N*-phenylethylenimine (3) Poly-β-propiolactone.

TABLE 3. CHARACTERISTIC PEAKS OF X-RAY DIFFRACTION DIAGRAMS OF THE POLYMERS

	2θ (°)				
Poly-*N*-phenylethylenimine	13.6	19.4	23.5		
Poly-β-propiolactone	21.2	29.2			
Copolymer	13.6	18.8	19.3	19.9	23.3

It is well known that β-propiolactone polymerizes by opening the ring between acyl-oxygen or alkyl carbon-oxygen bonds. In the copolymerization of *N*-phenylethylenimine with β-propiolactone,

TABLE 4. QUANTITY OF CARBOXYLIC ACID AND REDUCED VISCOSITY OF COPOLYMERS

		Copolymer	Graft copolymer
	Composition of copolymer (β-propiolactone mol%)	14.0	10.5
Before hydrolysis of copolymer	Quantity of carboxylic acid (g equivalent/g copolymer)	0.0	5.90×10^{-4}
	Reduced viscosity (d*l*/g)	0.828	0.173
After hydrolysis of copolymer	Quantity of carboxylic acid (g equivalent/g copolymer)	16.9×10^{-4}	17.0×10^{-4}
	Reduced viscosity (d*l*/g)	0.0943	0.127

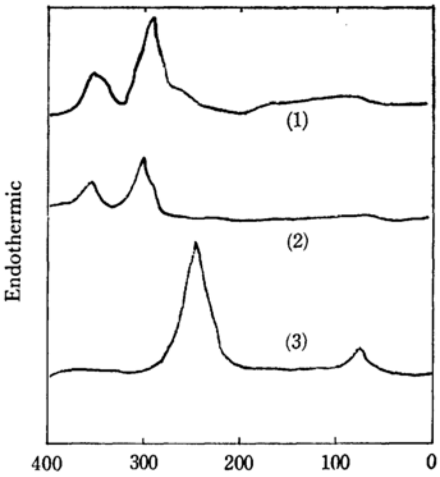
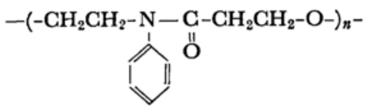


Fig. 4. Differential thermal analysis diagrams of the copolymer of *N*-phenylethylenimine and β-propiolactone, poly-*N*-phenylethylenimine, and poly-β-propiolactone.

(1) Copolymer of *N*-phenylethylenimine and β-propiolactone (β-propiolactone 31.8 mol%)
(2) Poly-*N*-phenylethylenimine
(3) Poly-β-propiolactone

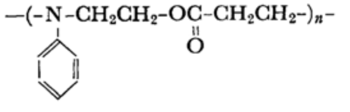
it is possible that the copolymer contains the following structures, according to the different modes of lactone-ring cleavage:

Cleavage of the acyl-oxygen bond:

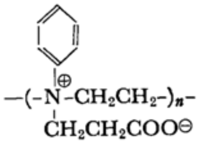


$$-(-CH_2CH_2-\underset{C_6H_5}{N}-\underset{\overset{\|}{O}}{C}-CH_2CH_2-O-)_n- \qquad (I)$$

Cleavage of the alkyl carbon-oxygen bond:



$$-(-\underset{C_6H_5}{N}-CH_2CH_2-O\underset{\overset{\|}{O}}{C}-CH_2CH_2-)_n- \qquad (II)$$



(III)

The absence of the characteristic peak of tertiary amide at 1650 cm^{-1} indicates that the copolymer does not contain the polyamide ether structure (I). Poly-*N*-phenylethylenimine and β-propiolactone could be reacted at 35°C to produce a branched polymer (III), but not at 0°C. The intrinsic viscosity and the carboxylic-group contents of the copolymer and the branched polymer are shown in Table 4.

The amount of the carboxyl group of the branched product was 5.90×10^{-4} g equivalent/g polymer, but no carboxylic group was present in the copolymer. This result indicates that the copolymer has not carboxyl group. It was observed that the amount of the carboxylic acid was equivalent to that of lactone present in the hydrolyzed product of the copolymer. The infrared spectrum of the hydrolyzed product displayed its peak at 1700 cm^{-1}, which was assigned to carboxyl bond, and the peak of the ester bond (1740 cm^{-1}) disappeared. The viscosity of the copolymer was depressed by the hydrolysis, whereas that of the branched copolymer was not changed. From these facts, it may be concluded that the copolymer contains the ester structure (II) in the main chain.

Monomer Reactivity Ratio. The relation

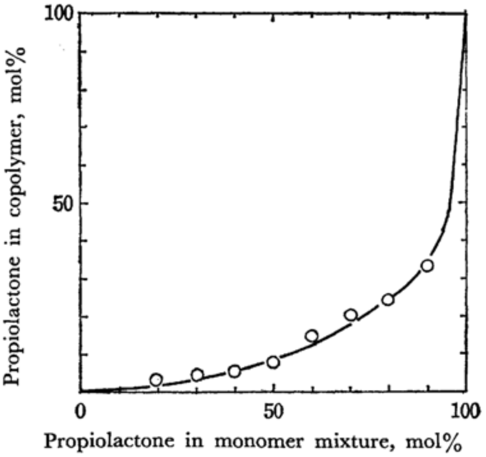


Fig. 5. Copolymerization of *N*-phenylethylenimine and β-propiolactone. Copolymer composition curve.

between the mole percentage of β-propiolactone in the copolymer and that in the monomer feed is shown in Fig. 5. From the curve, the monomer reactivity ratio of *N*-phenylethylenimine (r_1) and that of β-propiolactone (r_2) were estimated to be $r_1=7.5$ and $r_2=0.15$ respectively by the usual method.

The results show that *N*-phenylethylenimine reacted about 50 times as fast as β-propiolactone in this copolymerization, which gave a copolymer containing a small amount of the β-propiolactone. Further work on the mechanism of the initiation and propagation of this copolymerization will be reported in a subsequent paper.