BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3211—3215 (1969)

Crystalline Terpolymer of Formaldehyde, Carbon Dioxide, and *N*-Phenylethylenimine

Tsutomu KAGIYA and KŌZŌ NARITA
Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

and Masatsune KONDO
Sumitomo Chemical Co., Ltd., Takatsuki

(Received March 14, 1969)

Formaldehyde, carbon dioxide, and *N*-phenylethylenimine were allowed to terpolymerize by means of dimethyl ether acetate to give a crystalline solid terpolymer, melting at 178—265°C, with the composition of: CH_2O: 70—95, CO_2: 0.5—5, C_8H_9N: 5—25 mol%. The content of *N*-phenylethylenimine in the terpolymer thus obtained increased with the content of the imine in the feed, and that of carbon dioxide in the terpolymer, with the content of the imine in the feed, the lowering of the polymerization temperature, and the polymerization time. The infrared spectrum of the terpolymer showed the characteristic peaks of $-(-CH_2OCH_2O-)-$, $-(-O\overset{\overset{O}{\|}}{C}O-)-$ and $-(-N(C_6H_5)CH_2CH_2-)-$. The mechanism of the terpolymerization was proposed on the basis of these results.

Recently, the copolymerizations[1] of formaldehyde with olefins or with various aldehydes have been studied. No paper on the copolymerization of carbon dioxide as a monomer has, however, been reported.

The present authors have previously studied formaldehyde polymerization in a liquid carbon dioxide solution.[2] During the course of their study, the authors found that the crystalline terpolymers of formaldehyde, carbon dioxide, and *N*-phenylethylenimine were produced by dimethyl ether acetate.

In this paper, the sturcture and the physical properties of the terpolymer will be determined, and the mechanism of the terpolymerization will be discussed.

Experimental

Materials. The formaldehyde in liquid carbon dioxide was prepared by means of the two-step method reported previously.[2] Eighteen hundred grams of paraformaldehyde, 1000 g of polyethylene glycol (a degree of polymerization of about 10), and 1.8 mol of calcium carbonate were put into a 3000 m*l* decomposer, and then the mixture was heated at from 110 to 160°C under a carbon dioxide stream (flow rate: 160 m*l*/min). The mixture of formaldehyde and carbon dioxide was passed through two tubes cooled at −20°C and then liquefied in the monomer reservoir at −78°C. The *N*-phenylethylenimine was prepared according to the method of the literature[3] from *β*-bromoethylaniline hydrobromide; it was dried over sodium sulfate and fractionated twice before use (bp 70—70.5°C/13 mmHg). Commercial carbon dioxide was dried through two drying tubes packed with phosphorus pentoxide. The dimethyl ether acetate was prepared by the reaction[4] of monochloromethyl ether with potassium acetate; it was then purified by distillation (bp 117—118°C). The toluene, acetonitrile, and formic acid were purified in the usual way.

Polymerization Procedure. A 30 m*l* stainless steel autoclave or a 20 m*l* glass ampule was used as the reaction vessel. The vessel was degassed *in vacuo* and cooled at −198°C. Then, measured quantities of the catalyst and *N*-phenylethylenimine were put into the autoclave, and then a carbon dioxide solution of formaldehyde (about 60 wt%) or liquid formaldehyde was introduced. In the experiment using the glass ampule, a measured quantity of the organic solvent containing the catalyst, *N*-phenylethylenimine, and liquid formaldehyde was put into the ampule. The vessel was kept standing for the definite time at a constant temperature. After the reaction, the unreacted formaldehyde

1) C. Chachaty, *Compt. rend.*, **251**, 385 (1960); U.S. Pat. 2373561.

2) T. Kagiya, M. Kondo, K. Narita and K. Fukui, This Bulletin, **42**, 1688 (1969); T. Kagiya and K. Narita, *ibid.*, **42**, 2912 (1969).

3) H. W. Heine, B. L. Kapur and C. S. Match, *J. Am. Chem. Soc.*, **76**, 1173 (1954).

4) "Beilsteins Handbuch der Organischen Chemie," Band III, Deutschen Chemischen Gesellschaft, Julius Springer, Berlin (1921), p. 236.

TABLE 1. TERPOLYMERIZATION OF FORMALDEHYDE, CARBON DIOXIDE, AND *N*-PHENYLETHYLENIMINE

Expt. No.	Monomer (g, mol)			Polymerization condition*		Yield (g)	η_{sp}/c (dl/g)	Mp (°C)	Terpolymer composition (mol%)		
	CH_2O	CO_2	C_8H_9N	Temp. (°C)	Time (min)				CH_2O	CO_2	C_8H_9N
1	3.0 (0.10)	2.0 (0.045)	0.4 (0.0034)	10	60	1.77	8.38	178	95.0	0.5	4.5
2	6.0 (0.20)	4.0 (0.090)	1.2 (0.0100)	10	60	3.09	0.20	227	92.4	1.1	6.5
3	5.1 (0.170)	3.4 (0.077)	1.2 (0.0100)	10	1 day	3.25	1.60	206	87.0	3.3	9.7
4	6.6 (0.220)	4.4 (0.099)	1.2 (0.0100)	−20	60	2.31	0.20	269	89.7	3.6	6.9
5	5.1 (0.170)	3.4 (0.077)	1.2 (0.0100)	−78	60	0.56	0.19	270	80.0	4.3	15.7
6	4.8 (0.160)	3.2 (0.160)	3.1 (0.0260)	10	60	2.73	0.84	218	83.2	1.3	15.5
7	2.4 (0.080)	1.6 (0.036)	2.4 (0.0201)	10	60	2.16	0.16	225	73.9	2.5	23.6
8	0.6 (0.020)	0.4 (0.009)	4.8 (0.0402)	10	1 day	0.581	0.10	262	70.3	4.9	24.8

* Catalyst, dimethyl ether acetate 0.2 mmol.

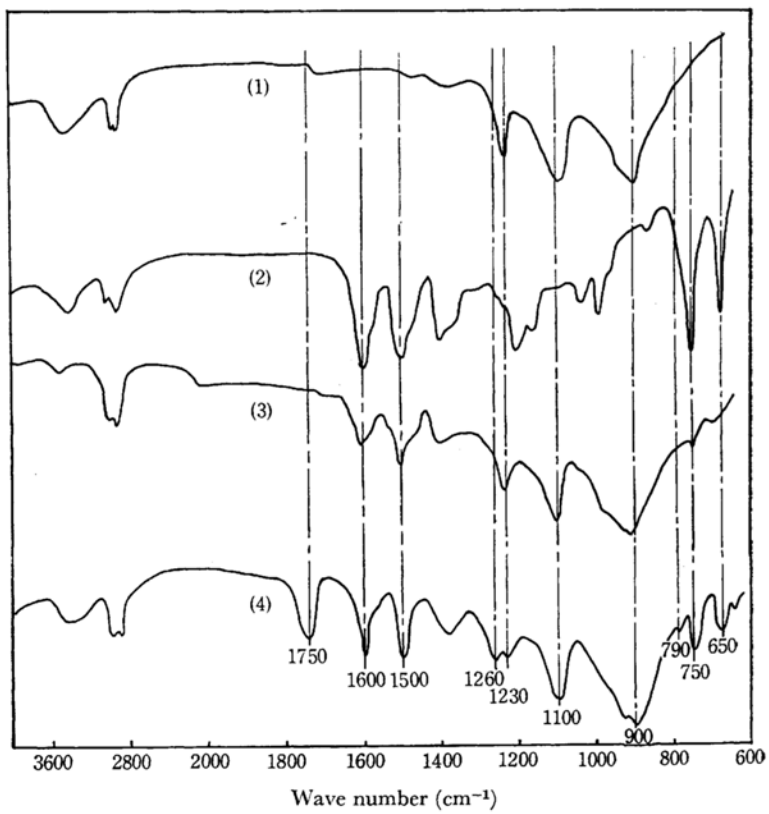


Fig. 1. Infrared spectra of: (1) poly-formaldehyde; (2) poly-*N*-phenylethylenimine; (3) copolymer of formaldehyde and *N*-phenylethylenimine; (4) terpolymer of formaldehyde, carbon dioxide, and *N*-phenylethylenimine.

and carbon dioxide were purged out, and the polymer was washed with cooled diethyl ether, dried *in vacuo* at room temperature, and weighed.

Analysis. The composition of the terpolymer was determined by elementary analysis. The specific viscosity measurement of the solution containing 0.5 g of the polymer in 100 m*l* of *p*-chlorophenol containing 2% α-pinene was carried out with the aid of an Ostwald viscometer at 60°C. The melting point of the polymer was visually determined in a nitrogen atmosphere in an electric heater. The infrared spectrum was obtained by using the potassium bromide pellet technique on a Japan Spectroscopic infrared spectrometer, Model DS-402G, with a sodium chloride prism. The X-ray diffraction diagram was recorded with a powder camera on a Shimadzu X-ray difractometer, Model GX-3B, employing Ni-filtered CuK_α radiation and standard techniques. The differential thermograms were obtained by using sandwiches with α-alumina powder as a diluent under an argon atmosphere on a Shimadzu differential thermal apparatus, Model DT-10, equipped with a platinum cell.

Results and Discussion

Terpolymerization of Formaldehyde, Carbon Dioxide, and *N*-Phenylethylenimine. The results of the terpolymerization of formaldehyde, carbon dioxide, and *N*-phenylethylenimine are shown in Table 1. Formaldehyde, being unable to copolymerize with carbon dioxide, was allowed to terpolymerize with carbon dioxide and *N*-phenylethylenimine in the presence of dimethyl ether acetate to give a white powdery polymer, which was soluble in *p*-chlorophenol, *m*-cresol, and dimethylformamide, and insoluble in diethyl ether, acetone, ethanol, chloroform, and toluene. The melting points of the terpolymers were 178°C to 265°C, between those of poly-*N*-phenylethylenimine (285—292°C) and poly-formaldehyde (*ca.* 170°C).

As is shown in Table 1, the *N*-phenylethylenimine content of the terpolymer increased with the imine content of the feed, and that of carbon dioxide in the terpolymer increased with the imine content of the feed, the lowering of polymerization temperature, and the polymerization time. The yield of the terpolymer increased with a rize in the reaction temperature.

Structure of the Terpolymer. The infrared spectrum of the resulting polymer showed the characteristic absorptions at 1230, 1100, and 900 cm^{-1} based on the acetal linkage (formaldehyde unit); at 1600, 1500, 750, and 690 cm^{-1} based on the benzene nucleus (*N*-phenylethylenimine unit), and at 1750, 1260, 1040, and 790 cm^{-1} based on the carbonate linkage (carbon dioxide unit) (Fig. 1). In addition, the infrared spectra of the polymers obtained by the polymerization of formaldehyde or *N*-phenylethylenimine in the presence of carbon dioxide and the copolymer of formaldehyde and *N*-phenylethylenimine in the absence of carbon dioxide are shown in Fig. 1. It is found that none of these polymers has the structure of the carbonate group $-(-OCO-)-$ (O).

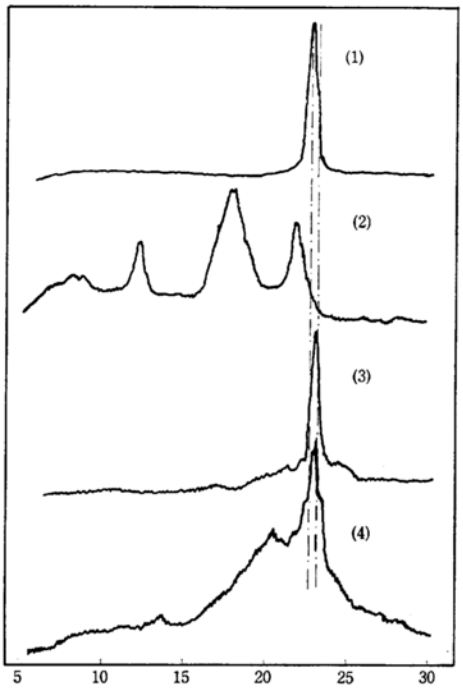


Fig. 2. X-Ray diffraction diagrams of: (1) poly-formaldehyde; (2) poly-*N*-phenylethylenimine; (3) copolymer of formaldehyde and *N*-phenylethylenimine; (4) terpolymer of formaldehyde, carbon dioxide, and *N*-phenylethylenimine.

Table 2. Characteristic peaks of X-ray diffraction diagrams of the polymers

	2θ (°)
Poly-formaldehyde	22.6
Poly-*N*-phenylethylenimine	8.3(s), 12.0, 18.0, 21.8
Copolymer of formaldehyde and *N*-phenylethylenimine	23.0, 24.2(s)
Terpolymer	13.5(s), 20.8(b), 23.0

(s) means small peak. (b) means broad peak.

X-Ray diffraction diagrams of the terpolymer (carbon dioxide 2.5 mol%, *N*-phenylethylenimine 23.6 mol%), the poly-*N*-phenylethylenimine, and poly-formaldehyde are shown in Fig. 2. The characteristic peaks (2θ) of these polymers are listed in Table 2. The X-ray diffraction diagram of the terpolymer displayed the main characteristic peak and a broad shoulder. The main characteristic peak of the terpolymer is the same as that of the copolymers of *N*-phenylethylenimine and formaldehyde, but a little different from the characteristic peaks of poly-formaldehyde and poly-*N*-phenyl-

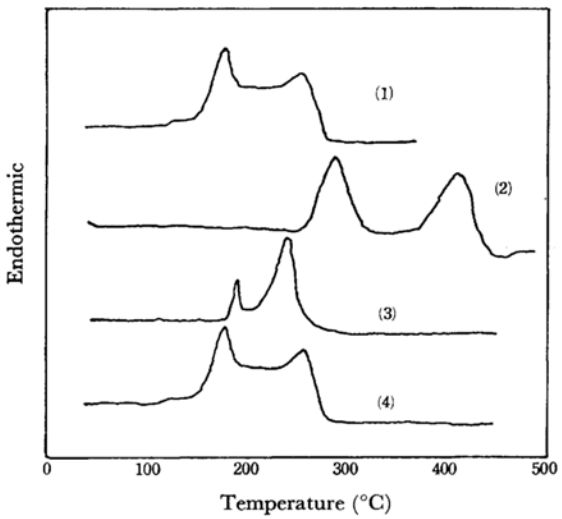


Fig. 3. Differential thermograms of: (1) polyformaldehyde; (2) poly-*N*-phenylethylenimine; (3) copolymer of formaldehyde and *N*-phenylethylenimine; (4) terpolymer of formaldehyde, carbon dioxide, and *N*-phenylethylenimine.

ethylenimine. On the other hand, the broad shoulder of the terpolymer is not different from the characteristic peaks of the above three polymers. It follows that the X-ray diagram indicates that the polymer from the three components contains a part of the block of the characteristic sequence of the terpolymer. In view of the relative half-value width, it may be concluded that the terpolymer is partially crystalline. Figure 3 shows a differential thermogram of the terpolymer (carbon dioxide 3.6 mol%, *N*-phenylethylenimine 6.7 mol%) in comparison with those of both homopolymers and those copolymers. The endothermic peak corresponds to the melting point of neither homopolymer, but a new peak of the terpolymer was observed.

Mechanism of the Terpolymerization. On the basis of the results shown in Table 1 and 3, the following reaction mechanism of the terpolymerization of formaldehyde, carbon dioxide, and *N*-phenylethylenimine by dimethyl ether acetate can be proposed.

Since formaldehyde was homopolymerized in the presence of carbon dioxide (Expt. No. 1 in Table 3), the reaction of formaldehyde with the propagating species of $-OCH_2^{\delta+}-^{\delta-}OOCCH_3$ (Eq. (1)) really occurs. On the other hand, from the fact that *N*-phenylethylenimine was hardly allowed to polymerize at all by dimethyl ether eacetate (Expt. No. 2 in Table 3), the reaction of *N*-phenylethylenimine with the propagating species of $-NCH_2CH_2^{\delta+}-^{\delta-}OOCCH_3$ (C_6H_5) is negligible in this polymerization.

On the other hand, formaldehyde was allowed to copolymerize with *N*-phenylethylenimine in

Table 3. Copolymerization of formaldehyde and *N*-phenylethylenimine

Expt. No.	Monomer (g, mol) CO_2	Monomer (g, mol) CH_2O	Monomer (g, mol) C_8H_9N	Catalyst (mol × 10^4)	Solvent[a]	Yield (g)	η_{sp}/c (dl/g)	Mp (°C)	The structures in the polymer obtained -(-CH_2O-)-	-(-NC_2H_4-)- (C_6H_5)	-(-OCO-)- (O)
1[c]	4.0 (0.090)	6.0 (0.200)	—	Dimethyl ether acetate 2	—	3.42	3.13	174	◎	—	—
2[c]	8.0 (0.108)	—	2.4 (0.0201)	Dimethyl ether acetate 2	—	0.03	—	—	—	◎	—
3[d]	—	—	1.2 (0.0100)	Formic acid 2	Acetonitrile	0.96	0.46[b]	285	—	◎	—
4[d]	—	1.7 (0.057)	0.6 (0.0050)	Dimethyl ether acetate 1	Toluene	0.52	3.32	180	◎	◎	—
5[d]	—	3.1 (0.103)	4.8 (0.0402)	Dimethyl ether acetate 1	Toluene	1.38	1.12	173	◎	◎	—
6[d]	—	1.1 (0.037)	0.6 (0.0050)	Dimethyl ether acetate 1	Acetonitrile	0.80	0.40	175	◎	◎	—
7[c]	—	3.6 (0.120)	3.2 (0.0402)	Dimethyl ether acetate 1	Toluene	2.85	0.82	172	◎	◎	—

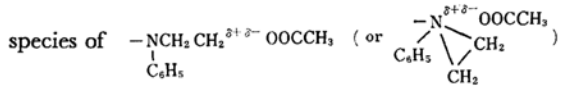
The polymerization temperature, 20°C; The polymerization time, 60 min.

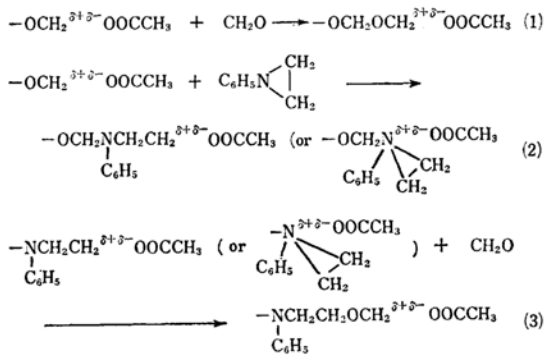
a) Solvent, 5 m*l*.

b) The viscosity was measured with 100 m*l* of the formic acid solution containing 0.5 g of the polymer.

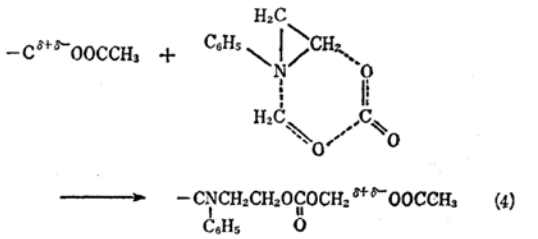
c) Reaction was carried out in a stainless steel autoclave.

d) Reaction was carried out in a glass ampule.

organic solvents by dimethyl ether acetate (Expts. No. 4, 5, 6, and 7 in Table 3). Therefore, both the reactions of *N*-phenylethylenimine with the propagating species of $-OCH_2^{\delta+}-^{\delta-}OOCCH_3$ (Eq. (2)) and of formaldehyde with the propagating species of  (Eq. (3)) may occur. From the results of both Expt. No. 2 in Table 1 and Expt. No. 1 in Table 3, it may be supposed that the rate of the propagation of reaction (1) is larger than that of reaction (2). On the basis of these results, the following elementary reactions may be proposed:



Further, carbon dioxide was allowed by dimethyl ether acetate to react only with formaldehyde in the presence of *N*-phenylethylenimine to give a terpolymer. The infrared spectrum of the terpolymer showed the existence of $-(-OCH_2OCH_2-)-$, $-(-NCH_2CH_2-)-$, and $-(-OCO-)-$. Therefore, it may be considered that the existence of carbon dioxide in this terpolymer is caused by the attack of the complex of formaldehyde, carbon dioxide, and *N*-phenylethylenimine on the propagating species of $-CH_2^{\delta+}-^{\delta-}OOCCH_3$ as follows:



The low carbon dioxide content (0.5—5 mol%) in the terpolymer indicates that the equilibrium constant of the reaction (4) is very small. This quantitative mechanism is consistent with the experimental results. A detailed study of the mechanism of this type of terpolymerization is now being carried out and will be reported on in a subsequent paper.

The authors wish to express their gratitude to Professor Kenichi Fukui for his helpful suggestions and to Mr. Hiroshi Hatta for his assistance in carrying out the experiments.