

## The Copolymerization Characteristics of Vinylene Carbonate, $\gamma$ -Crotonolactone and Methyl Bicyclo(2,2,1)-2-heptene-5-carboxylate

JOSEPH M. JUDGE\* and CHARLES C. PRICE, *Departments of Chemistry, Universities of Notre Dame and Pennsylvania, South Bend, Indiana, and Philadelphia, Pennsylvania*

In general, 1,2-disubstituted monomers are extremely unreactive in free radical copolymerization. Among the more reactive are such cyclic monomers as maleic anhydride, vinylene carbonate,<sup>1</sup> and indone.<sup>2</sup> It was the purpose of the present investigation to determine the copolymerization characteristics of a few cyclic monomers.

### EXPERIMENTAL

*Vinylene carbonate* was prepared according to the procedure of Newman and Addor.<sup>1</sup> *Chloroethylene carbonate* was first prepared by passing a stream of dry chlorine slowly into 305 g. (3.41 moles) of freshly distilled ethylene carbonate b.p. 152° (30 mm.), until a weight increase of 119 g. was obtained. The chlorination was carried out at 65–75° in the presence of ultraviolet light from a General Electric mercury vapor lamp.

Distillation under reduced pressure, after removal of excess chlorine and hydrogen chloride from the reaction mixture by a stream of dry air, yielded 7 g. of 1,2-dichloroethylene carbonate, b.p. 78–80° (20 mm.) and 258 g. (61%) of the desired chloroethylene carbonate, b.p. 121–123° (18 mm.),  $n_D^{20} = 1.4555$ .

Further distillation of the fore-run yielded pure 1,2-dichloroethylene carbonate, b.p. 78–79° (19 mm.),  $n_D^{20} = 1.4631$ .

*Dehydrochlorination* was accomplished by adding a solution of 169 g. of triethylamine in 50 ml. of anhydrous ethyl ether slowly over a twelve-hour period to a refluxing, stirred solution of 200 g. of chloroethylene carbonate and 0.5 g. of triethylamine hydrochloride in 250 ml. of anhydrous ethyl ether. After all the amine had been added, the stirring and refluxing were continued for an additional thirty-three hours. A large amount of a dark brown solid precipitated during the amine addition and subsequent stirring.

The reaction mixture was cooled and filtered through a sintered glass Buchner funnel. The solids were washed with three 100-ml. portions of anhydrous ethyl ether, and the washings were added to the filtrate. The

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washed solid weighed 200 g. and was essentially triethylamine hydrochloride.

By careful distillation through a 40-cm. helix-packed column equipped with a total-reflux, partial-takeoff head, the ether was removed. Final fractional distillation yielded 53 g. (38% of vinylene carbonate, b.p. 74–75° (34 mm.), m.p. 20.5°,  $n_D^{26} = 1.4183$ . Literature values are b.p. 74–76° (33 mm.), m.p. 21°,  $n_D^{20} = 1.4190$ .)

### Methyl Bicyclo(2,2,1)-2-heptene-5-carboxylate<sup>3</sup>

A solution of 89.2 g. of freshly-distilled cyclopentadiene, 130 g. of re-distilled methyl acrylate (b.p. 79°), 1.0 g. of hydroquinone, and 200 ml. of anhydrous ethyl ether was stirred at 0–5° for four hours.

The reaction was allowed to warm to room temperature, and was distilled to remove unreacted monomers and solvent. The residue was fractionally distilled through a 40-cm. glass-helix packed column. A colorless liquid with a sickening sweet odor was obtained, b.p. 63.5° (5 mm.),  $n_D^{25} = 1.4718$ , yield, 176 g. (86%). Literature values<sup>3</sup> are: b.p. 63° (5 mm.),  $n_D^{25} = 1.4718$ .

### Methyl Vinyl Sulfide

To a molten slurry of potassium hydroxide was added cautiously 75 g. of  $\beta$ -hydroxyethyl methyl sulfide. A reaction temperature of 220–240° was maintained with the aid of a paraffin wax bath.<sup>4b</sup> A distillate composed of two layers was slowly collected during the reaction. The aqueous phase was separated, and the sulfide layer dried over anhydrous magnesium sulfate. Fractional distillation gave 25 g. of methyl vinyl sulfide, b.p. 68–69°,  $n_D^{25} = 1.4820$ . (Literature:<sup>4</sup> b.p. 66–67°,  $n_D^{20} = 1.4833$ .)

### $\gamma$ -Crotonolactone

$\alpha$ -Bromobutyrolactone<sup>5</sup> was prepared by treating a slurry of 13.4 g. of red phosphorus in 100 g. of  $\gamma$ -butyrolactone with 80 g. of bromine added slowly over a half-hour period, the reaction mixture being stirred and kept cool (below 20°). A vigorous reaction occurred. After the addition, the reaction mixture was heated to 80° by means of a water bath, and 195 g. of bromine was added slowly over a half-hour period. The reaction mixture was maintained at 80°, stirred for four hours to complete the reaction, and then cooled.

Air was drawn through the mixture until the deep red color had disappeared (this required four hours). To the bromine-free solution was added 25 ml. of water, the solution being heated to 80° before the addition. After cessation of the vigorous reaction the mixture was poured, *in toto*, into 300 ml. of water and refluxed for four hours. A heavy liquid layer was separated from the aqueous phase. The top layer was *carefully* neutralized with sodium carbonate (care must be taken to avoid the spray, since the reaction products are vesicants) and extracted with three 50-ml.

portions of ethyl ether. The lower layer and ether extracts were combined, dried over anhydrous magnesium sulfate for twelve hours, and vacuum-distilled. A heavy water-white liquid was obtained, b.p.  $125^{\circ}$  (14 mm.),  $n_D^{25} = 1.5030$ . The yield was 124 g. (70%).

*Dehydrobromination* of 83 g. (0.5 mole) of  $\alpha$ -bromobutyrolactone in 200 ml. of refluxing anhydrous ethyl ether was effected by slowly adding a solution of 61 g. of triethylamine in 50 cc. of anhydrous ethyl ether. The addition required five hours. Stirring and refluxing were continued for an additional thirty hours.

The precipitated triethylamine hydrochloride was separated by vacuum filtration, and the ether removed by distillation. The liquid residue was vacuum-distilled, and 25 g. (60%) of  $\gamma$ -crotonolactone was obtained, b.p.  $94-98^{\circ}$  (14 mm.),  $n_D^{25} = 1.4604$ , m.p.  $5^{\circ}$ .

A phenylhydrazine derivative was prepared, m.p.  $184.5^{\circ}$ . The literature reports:<sup>6</sup>  $\gamma$ -crotonalactone, b.p.  $80-86^{\circ}$  (7 mm.), m.p.  $5^{\circ}$ ; phenylhydrazide derivative, m.p.  $183.5^{\circ}$ .

### Copolymerization

Monomer mixtures containing a total of 0.08 mole of monomers were made up over a range of mole ratios from 20:80 to 80:20. The mixtures were placed in glass tubes containing 0.2 mole-% (0.021 g.) of azoisobutyronitrile, the tubes were flushed with nitrogen, evacuated, sealed, and

TABLE I  
Copolymerization of Vinylene Carbonate ( $M_2$ ) with Vinyl Acetate ( $M_1$ )<sup>a</sup>  
( $r_1 = 7.3 \pm 0.7$ ,  $r_2 = 0.13 \pm 0.1$ ;  $Q_2 = 0.002$ ,  $e_2 = -0.73$ )

$M_2^b$	Time, hr.	Conversion, %	C, %	H, %	$m_2^c$
0.1942	0.5	3.0	55.36	6.82	0.032
0.4015	1.5	4.5	54.48	6.35	0.096
0.5027	2.0	5.0	54.42	6.80	0.098
0.5969	2.0	4.0 <sup>d</sup>	53.65	6.02	0.155
0.6070	2.0	3.0	53.57	7.07	0.160
0.8108	7.0	6.0	50.43	5.61	0.385

<sup>a</sup> These copolymers were isolated, and purified by multiple precipitations from dilute acetone solution by ethyl ether. The white polymeric material was dried for sixteen hours at  $45^{\circ}$  under 0.1 mm. vacuum.

<sup>b</sup> Mole fraction of vinylene carbonate in monomer mixture.

<sup>c</sup> Mole fraction of vinylene carbonate in copolymer, as calculated from carbon content.

<sup>d</sup> Specific viscosity of a 1.0% solution in chloroform was 0.34.

heated to  $60 \pm 0.5^{\circ}$  for a predetermined time interval. All polymerizations were stopped at low conversions (less than 8%). The tubes were cautiously opened, and the contents were slowly poured into a large excess of a vigorously stirred, cold precipitant.

TABLE II  
Copolymerization of Vinylene Carbonate ( $M_2$ ) with Methyl Vinyl Sulfide ( $M_1$ )<sup>a</sup>  
( $r_1 = 10.6 \pm 1.2$ ,  $r_2 = 0.05 \pm 0.04$ ;  $Q_2 = 0.01$ ,  $e_2 = -0.71$ .)

$M_2^b$	Time, hr.	Conversion, %	C, %	H, %	S, %	$m_2^c$
0.2020	22	7.1	48.62	7.85	42.21	0.020
0.3009	14	3.3	48.28	7.42	40.51	0.053
0.5016 <sup>d</sup>	22	5.0	49.69	7.24	38.55	0.088
0.5985	14	2.3	48.05	7.16	35.32	0.161
0.7018	22	6.8	47.30	6.99	35.52	0.157
0.8009	23	7.2	48.14	6.64	32.35	0.224

<sup>a</sup> These copolymers were precipitated as above, and purified by a freeze-drying technique from dilute benzene solution. The copolymers were white solids and were electrostatically charged.

<sup>b</sup> Mole fraction of vinylene carbonate in monomer mixture.

<sup>c</sup> Mole fraction of vinylene carbonate in the copolymer as calculated from the sulfur analysis.

<sup>d</sup> Per cent carbon greater than that for 100% methyl vinyl sulfide.

TABLE III  
Copolymerization of Vinylene Carbonate ( $M_2$ ) with Styrene ( $M_1$ )<sup>a</sup>  
( $r_1 \approx 8-20$ ,  $r_2 = 0$ )

$M_2^b$	Time, hr.	Conversion, %	C, %	H, %	$m_2^c$
0.1983	2.0	5.4	91.81	7.78	0.010
0.4010	2.5	6.0	91.96	7.75	0.006
0.5000	2.5	5.2 <sup>d</sup>	91.73	7.92	0.015
0.6001	2.5	4.3	91.35	8.22	0.021

<sup>a</sup> These copolymers were isolated by precipitation from benzene by cold methanol, and purified by freeze-drying from dilute benzene solution.

<sup>b</sup> Mole fraction of vinylene carbonate in the monomer mixture.

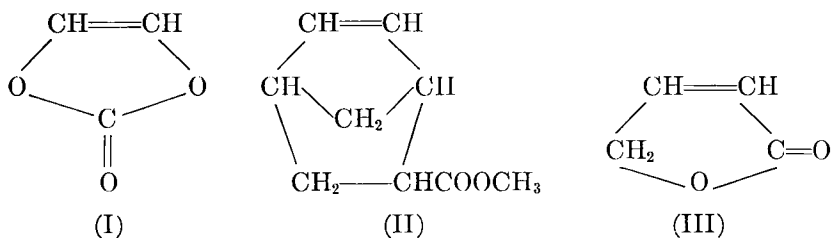
<sup>c</sup> Mole fraction of vinylene carbonate in the copolymer, as calculated from the carbon content.

<sup>d</sup> Specific viscosity of a 1% solution in benzene was 0.43.

The precipitated polymers were isolated, freed from occluded monomer, dried, and submitted for elemental quantitative analysis (Galbraith Laboratories, Knoxville, Tenn.). The results are summarized in Tables I-VI.

## DISCUSSION

The general low reactivity of 1,2-disubstituted ethylenic monomers in homopolymerization and copolymerization has been ascribed to steric factors.<sup>8-10</sup> In the hope that cyclic analogs would be less hindered, we have investigated three cyclic compounds with a 1,2-disubstituted double bond: vinylene carbonate (I), methyl bicyclo (2,2,1)-2-heptene-5-carboxylate (II) and  $\gamma$ -crotonolactone (III).



(I) has been prepared by Newman and Addor,<sup>1</sup> and we prepared it by following their procedure of chlorination and dehydrochlorination of ethylene carbonate.

(II) was prepared readily by Diels-Alder addition of methyl acrylate to cyclopentadiene.<sup>3</sup>

There was no satisfactory preparation of (III) mentioned in the literature. We found that bromination of  $\gamma$ -butyrolactone, followed by triethylamine dehydrobromination, afforded the desired lactone in 42% overall yield.

Copolymerization of (I) with reactive monomers, such as styrene and methyl methacrylate, gave polymer with very little incorporation of (I). For example, a styrene mixture containing 70 mole-% (I) gave polystyrene with no more than 2 mole-% of (I) units. Acrylonitrile and vinylidene chloride gave copolymer, but the copolymer precipitated and therefore these systems could not be used for evaluation of copolymerization characteristics. Copolymerization with vinyl acetate and methyl vinyl sulfide proceeded satisfactorily. The data are summarized in Tables I, II, and VII. The monomer reactivity factor  $Q$  is about the same as or slightly less than that for vinyl acetate ( $Q = 0.01$ ). The electrical factor ( $e = -0.7$ ) is slightly more negative than for vinyl acetate ( $e = -0.5$ ). This could be explained by the fact that resonance, as indicated in (Ia), (Ib),

TABLE IV  
Copolymerization of Methyl Bicyclo(2,2,1)-2-heptene-5-carboxylate ( $M_2$ ) with Vinyl Acetate ( $M_1$ )<sup>a</sup>  
( $r_1 = 1.5 \pm 0.24$ ,  $r_2 = 0.45 \pm 0.07$ ;  $Q_2 = 0.01$ ,  $e_2 = 0.1$ )

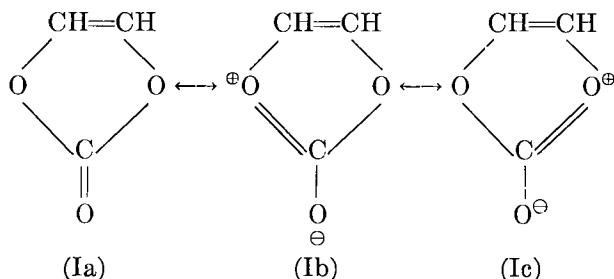
$M_2^b$	Time, hr.	Conversion, %	C, %	H, %	$m_2^c$
0.1972	15.5	5.2	59.70	7.46	0.163
0.3949	15	1.5	61.43	7.47	0.249
0.5000	20	4.8	62.81	7.64	0.253
0.6005	20	1.9	64.55	7.96	0.437
0.6970	15	1.5	66.23	6.87	0.554

<sup>a</sup> These copolymers were precipitated from benzene by petroleum ether, and purified by freeze-drying from dilute benzene solution.

<sup>b</sup> Mole fraction of bicyclic monomer in monomer mixture.

<sup>c</sup> Mole fraction of bicyclic monomer in copolymer, as calculated from carbon content.

and (Ic), would place a smaller positive charge on either oxygen in (I) than similar resonance would for the oxygen of vinyl acetate.



These results are in accord with those reported by Hayashi and Smets,<sup>10</sup> who studied the copolymerization of (I) with vinyl acetate, vinyl chloride, vinyl pyrrolidone, and methyl methacrylate. They proposed values of  $Q = 0.012$  and  $e = -0.60$ .

The copolymerization characteristics for (II), determined from experiments with vinyl acetate and acrylonitrile, are summarized in Tables IV, V, and VII. The monomer reactivity factor  $Q$  appears to be equal to or perhaps slightly greater than that for a vinyl acetate ( $Q = 0.01$ ). The values of  $Q$  for (I) and (II) suggest that the low reactivity of these monomers is not the result of steric hindrance but is a consequence of virtually no resonance stabilization of the new radical adduct formed from them.

TABLE V  
Copolymerization of Methyl Bicyclo(2,2,1)-2-heptene-5-carboxylate ( $M_2$ ) with  
Acrylonitrile ( $M_1$ )<sup>a</sup>  
( $r_1 = 1.5 \pm 0.5$ ,  $r_2 = 0.2 \pm 0.1$ ;  $Q_2 = 0.05$ ,  $e_2 = -0.1$ .)

$M_2^b$	Time, hr.	Conver- sion, %	C, %	H, %	N, % <sup>c</sup>	$m_2^d$
0.1978	11.8	8.0	67.53	6.44	17.24	0.1463
0.3001	13.5	4.0	67.26	6.66	16.20	0.1801
0.5000	13	1.0 <sup>e</sup>	67.41	7.03	13.65	0.235
0.5975	68	0.8 <sup>f</sup>	67.66	6.92	11.92	0.287
0.0000	—	0.8 <sup>g</sup>	67.64	5.98	25.34	—

<sup>a</sup> It was necessary to run these reactions in *N,N*-dimethylformamide. To the monomer mixture was added 3.0 ml. of dimethylformamide. The copolymers were isolated by multiple precipitations into methanol from dimethylformamide solution. The polymers were dried at 30° and 0.05 mm. They were faintly yellow solids.

<sup>b</sup> Mole fraction of bicyclic monomer in monomer mixture.

<sup>c</sup> Nitrogen analysis is uncorrected.

<sup>d</sup> Mole fraction of bicyclic monomer in copolymer, as calculated from nitrogen analysis.

<sup>e</sup>  $\eta_{sp} = 0.22$  (1.0% solution in dimethylformamide).

<sup>f</sup> Soluble in acetone, unlike the other copolymers in this series.

<sup>g</sup> Polyacrylonitrile made in dimethylformamide and given same purification treatment as copolymers.

TABLE VI  
Copolymerization of Crotonolactone ( $M_2$ ) with Styrene ( $M_1$ )<sup>a</sup>  
( $r_1 = 8.5 \pm 5.0$ ,  $r_2 = 0$ )

$M_2^b$	Time, hr.	Conversion, %	C, %	H, %	$m_2^c$
0.2005	2	3	89.69	7.67	0.073
0.3985	4.5	5.2	90.52	7.72	0.049
0.5016	4	10 <sup>d</sup>	89.29	7.59	0.084
0.6015	4.5	4	89.56	7.70	0.077
0.7975	5	10	86.83	7.11	0.154

<sup>a</sup> These copolymers from this system were precipitated from dilute benzene solution by cold methanol, then purified by freeze-drying from benzene solution. They were white solids.

<sup>b</sup> Mole fraction of crotonolactone in monomer mixture.

<sup>c</sup> Mole fraction of crotonolactone in copolymer.

<sup>d</sup> Specific viscosity of a 1% solution in benzene was 0.43.

TABLE VII  
Summary of Copolymerization Characteristics for Vinylene Carbonate (I) and Methyl Bicyclo(2,2,1)-2-heptene-5-carboxylate (II)

$M_1$	$M_2$	$r_1$	$r_2$	$Q_2$	$e_2$
Vinyl acetate <sup>a</sup>	I	$7.3 \pm 0.7$	$0.13 \pm 0.1$	0.002	-0.7
Vinyl methyl sulfide <sup>b</sup>	I	$10.6 \pm 1.2$	$0.05 \pm 0.04$	0.01	-0.7
	I			0.005	-1.1 <sup>c</sup>
Vinyl acetate <sup>a</sup>	II	$1.5 \pm 0.24$	$0.45 \pm 0.07$	0.01	0.1
Acrylonitrile <sup>d</sup>	II	$1.5 \pm 0.5$	$0.2 \pm 0.1$	0.05	-0.1
	II			0.005	-0.1 <sup>c</sup>

<sup>a</sup>  $Q_1 = 0.01$ ,  $e_1 = -0.5$  (see ref. 7, p. 240).

<sup>b</sup>  $Q_1 = 0.34$ ,  $e_1 = -1.5$  (ref. 4a).

<sup>c</sup> By solving the equations  $r_1 = (Q_1/Q_2) \exp \{-e_1(e_1 - e_2)\}$  and  $r_1' = (Q_1'/Q_2) \exp \{-e_1'(e_1' - e_2)\}$ .

<sup>d</sup>  $Q_1 = 0.44$ ,  $e_1 = 1.2$  (see ref. 7, p. 241).

The electrical factor for (II) ( $e \simeq 0.0$ ) is appreciably different from that for vinyl acetate ( $e = -0.5$ ) and can be readily accounted for only by an appreciably electron-withdrawing inductive effect of the ester group, passed through the two saturated atoms interposed between the ester group and the vinylene group.

$\gamma$ -Crotonolactone (III) proved to be a very poor monomer. It seems likely that the two  $\gamma$ -hydrogens in this molecule may be too readily removed in a degradative chain-transfer process. The resulting radical would be well stabilized by resonance.

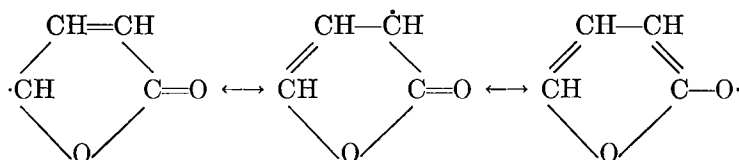
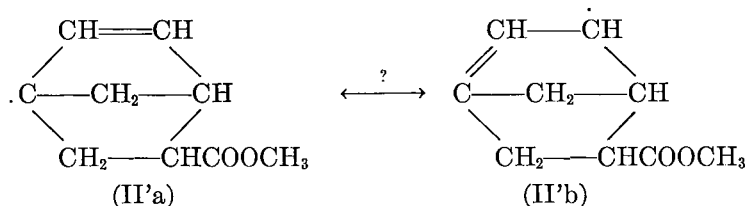


TABLE VIII  
 Principal Infrared Absorption Bands

Vinylene carbonate		$\alpha$ -Bromo- $\gamma$ -butyrolactone		$\gamma$ -Crotonolactone	
$\lambda$	% Abs.	$\lambda$	% Abs.	$\lambda$	% Abs.
3.15	65	3.40	14	3.25	10
4.67	31	5.62	93	3.40	15
5.01	40	6.76	25	5.64	94
5.19	34	6.95	25	5.75	92
5.41	98	7.27	48	6.25	33
5.47	99	8.21	60	6.92	39
5.57	98	8.34	64	7.28	34
5.64	91	8.55	75	7.42	38
6.42	27	8.65	76	7.50	35
6.92	58	9.50	27	8.67	80
8.64	97	9.70	60	9.15	65
9.10	97	9.83	49	9.70	75
9.27	97	10.10	60	10.10	40
11.07	54	11.25	40	11.39	55
11.25	46			12.36	68
12.88	37				
13.50	80				
14.05	90				

Similar chain transfer in (II) would presumably be unlikely because of the extremely unfavorable geometry of the hypothetical resonance structures [(II'b) violates Bredt's rule].



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### Synopsis

The copolymerization of three cyclic vinylene monomers has been investigated. For vinylene carbonate, we found  $Q = 0.005$ ,  $e = -0.8$ , and for methyl bicyclo(2,2,1)-2-heptene-5-carboxylate,  $Q = 0.02$ ,  $e = 0.0$ . A convenient preparation of  $\gamma$ -crotonolactone is reported, but no satisfactory copolymerization for this material was found.

### Résumé

On a étudié la copolymérisation de trois monomères cycliques du type vinylène. Pour le carbonate de vinylène, nous trouvons  $Q = 0.005$ ,  $e = -0.8$  et pour le méthylbicyclo(2,2,1)-2-heptène-5-carboxylate,  $Q = 0.02$ ,  $e = 0.0$ . On décrit une méthode convenable de préparation de la  $\gamma$ -crotonolactone, mais on n'a pas trouvé de copolymérisation satisfaisante pour ce matériau.

### Zusammenfassung

Die Copolymerisation von drei cyclischen Vinylenmonomeren wurde untersucht. Für Vinylencarbonat wurde  $Q = 0,005$ ,  $e = -0,8$  und für Methylbicyclo-(2,2,1)-2-hepten-5-carboxylat  $Q = 0,02$ ,  $e = 0,0$  gefunden. Eine bequeme Darstellung für  $\gamma$ -Crotonolacton wird angegeben, es konnte aber keine befriedigende Copolymerisation dieses Stoffes erreicht werden.

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