The Preparation and Polymerization of Divinyl Carbonate*

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Since Butler[1] found the principle of the intra-inter polymerization of divinyl compounds, many divinyl compounds have been reported to undergo cyclopolymerization, yielding soluble polymers.

Divinyl carbonate seems, considering its structural analogy to divinyl thiocarbonate,[2] to be a monomer with the possibility of cyclopolymerization. The hydrolysis of the cyclized polymer might yield polyvinyl alcohol, which in turn might show some features of the cyclopolymer with stereoregularity.[3] The present study started from such point of view.

Divinyl carbonate has not previously been successfully prepared. In the present paper we wish to report the synthesis of divinyl carbonate and its polymerization, emphasis being laid on the cyclopolymerization of the monomer under various conditions. The identification of cyclic units in the polymer and the estimation of the degree of cyclization have been made by means of infrared analysis based on the study of model compounds.

Experimental

The Preparation of Divinyl Carbonate.—Divinyl carbonate was synthesized by the reaction of mercuridiacetaldehyde with phosgene in tetrahydrofuran. A mixture of 220 g. of mercuridiacetaldehyde,[4] 150 ml. of tetrahydrofuran, and 0.5 g. of hydroquinone was placed in a 500 ml. three-necked flask equipped with a reflux condenser with a calcium chloride tube, a stirrer and a glass gas inlet tube, the flask was then cooled with an ice bath. Phosgene (29 ml.), which had been condensed in a graduated trap cooled in a dry ice - acetone bath, was gradually evaporated through a phosphorus pentoxide tube into the flask while its contents were being stirred. The flask was then kept at 0°C for 1 hr. while being stirred, kept at room temperature for another hour, and then warmed slowly up to 60°C. The reaction, which was not complete at 0°C, yielded vinyl chlorocarbonate as a main product. The volatile components of the reaction mixture were collected by vacuum distillation at room temperature, and then the distillate was subjected to fractional distillation at reduced pressure using a fractional column of about 30 theoretical plates. The yield was 17 g., 40% based on mercuridiacetaldehyde. Colorless liquid, b. p. 103.5—104.5°C, 49.0—49.2°C/98 mmHg, m. p. -38.0—-38.5°C, n_D^{25} 1.4135, d_4^{25} 1.0095.

Found: C, 51.92; H, 5.22. Calcd. for $C_5H_6O_3$: C, 52.63; H, 5.25%.

The Synthesis of Carbonates. — Trimethylene carbonate was prepared by a known method[5] from 45 g. of diethyl carbonate, 25 g. of 1,3-propanediol and 0.2 g. of sodium. B. p. 115—116°C/2 mmHg; m. p. 47.0—47.5°C (recrystallized from ether). Yield 27%.

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[1] G. B. Butler and R. J. Angelo, *J. Am. Chem. Soc.*, **79**, 3128 (1957).

[2] H. R. Ringsdorf and C. G. Overberger, *Makromol. Chem.*, **44/46**, 418 (1961).

[3] S. Murahashi, H. Yuki, T. Sano, U. Yonemura, H. Tadokoro and Y. Chatani, *J. Polymer Sci.*, **62**, 577 (1964).

[4] A. N. Nesmeyanov, R. M. Khomtov and I. F. Lutsenko, *Izvest. Akad. Nauk SSSR., Otdel. Khim. Nauk*, **1957**, 942.

[5] L. Hough and J. E. Priddle, *J. Chem. Soc.*, **1961**, 581.

2, 3-Butanediol cyclic carbonate was prepared from 25 g. of 2, 3-butanediol, 45 g. of diethyl carbonate and 0.1 g. of sodium. The mixture was then heated for 5 hr. at 120°C, the ethanol thus formed being distilled through a Vigreux column. After the distillation of ethanol had ceased, the reaction mixture was distilled under reduced pressure twice, thus yielding 19 g. of the product (60%), b. p. 78—79°C/4 mmHg.

Found: C, 51.78; H, 6.88. Calcd. for $C_5H_8O_3$: C, 51.72; H, 6.89%.

2, 4-Pentanediol cyclic carbonate was prepared in a manner similar to that used for 2, 3-butanediol cyclic carbonate, using 10 g. of 2, 4-pentanediol, 15 g. of diethyl carbonate and 0.1 g. of sodium. The yield was 7 g. (54%). B. p. 129—130°C/7 mmHg, m. p. 12.5—13.0°C.

Found: C, 55.37; H, 7.78. Calcd. for $C_6H_{10}O_3$: C, 55.39; H, 7.75%.

For the preparation of ethyl vinyl carbonate, a mixture of 60 g. mercuridiacetaldehyde, 15 g. of ethyl chlorocarbonate and 30 ml. of tetrahydrofuran was stirred in a three-necked flask equipped with a reflux condenser and a stirrer, first at room temperature for several hours, and then at gradually increased temperatures up to 65°C. The volatile component of the reaction mixture was collected in a trap cooled by a dry ice - acetone bath in a vacuum, and then fractionally distilled, yielding 11 g. of the product (69%), b. p. 71—72°C/176 mmHg.

Found: C, 50.98; H, 6.75. Calcd. for $C_5H_8O_3$: C, 51.72; H, 6.89%.

Propylene carbonate, a commercial product, was used after distillation and the gas chromatographic comfirmation of its purity.

The solvents for the polymerization experiments were purified by standard procedures.

Polymerization.—An ampoule containing a monomer, a solvent and benzoylperoxide (0.5 mol.% of the monomer) or 2, 2′-azobisisobutyronitrile was degassed three times in a high-vacuum manipulation and then sealed. Polymerization was carried out in a thermostat at 60±0.05°C.

In the photo-sensitized polymerization, a solution of the monomer and 2, 2′-azobisisobutyronitrile in benzene was irradiated with a ultraviolet lamp (Toshiba SHL 100-UV) in a vacuum, using a vessel with a fused silica window.

After polymerization, a small amount of an inhibitor, *p*-*t*-butylcatechol, was introduced into the polymerization mixture, and then the residual monomer and the solvent are stripped in a vacuum at room temperature. The residual crude polymer was treated with acetone. The acetone-soluble fraction was precipitated with petroleum ether. In some experiments the polymerization mixture was poured into a large amount of hexane, yielding a precipitate of the polymer. The polymer was dried at room temperature in vacuo.

A typical example of the analysis of the polymer is shown below for the sample of Exp. No. 1 in Table V.

Found: C, 52.61; H, 5.29. Calcd. for $C_5H_6O_3$: C, 52.62; H, 5.31%.

Infrared Spectra.—The absorption coefficients of the model compounds were determined in chloroform, as it was confirmed that the Lambert-Beer law was applicable at concentrations from 0.02 to 0.5 mol./l. The infrared spectra of the polymer were taken by the KBr-tablet method.

Results

The Infrared Analysis of the Polymer Structure.—An infrared spectrum of the polymer, shown in Fig. 1, has two carbonyl absorptions, at 1810 and 1760 cm^{-1}, and a double bond absorption at 1660 cm^{-1}. To identify these absorptions, the infrared spectra of model compounds were studied, they are listed in Table I. It can there be seen that the band at 1810 cm^{-1} in the polymer corresponds to 2, 3-butanediol cyclic carbonate (1810) and closely corresponds to propylene carbonate (1800), thus indicating that the 1810 band may be due to the presence of a 5-membered carbonate. The band at 1760 cm^{-1} of the polymer corresponds to 2, 4-pentanediol cyclic carbonate (1750), trimethylene carbonate (1755), and also to ethyl vinyl carbonate (1760), indicating that this band may originate from the unsaturated carbonate of 1, 2-addition type, presumably being overlapped with a 6-membered cyclic carbonate. Thus, the structure of the polymer may be represented by Formula I:

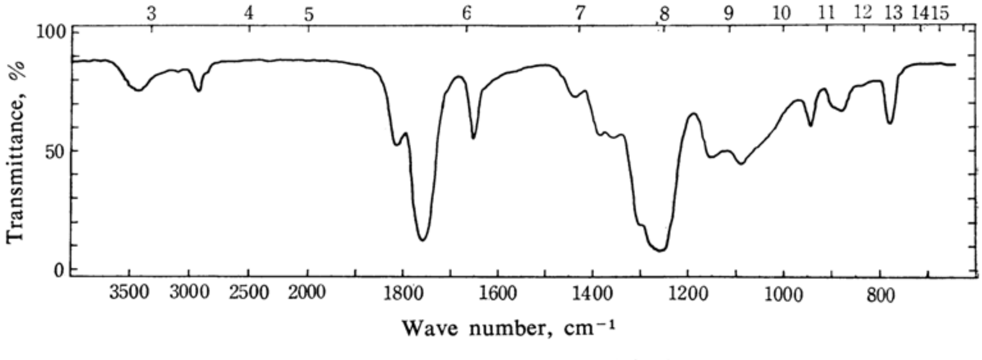
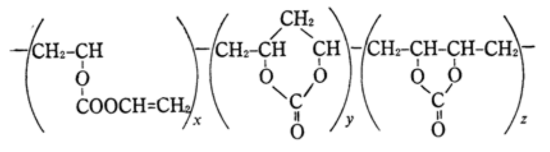


Fig. 1. Infrared spectrum of polydivinylcarbonate.



I

Using the following notations:

Polymer structure	Molar concn.	Absorption coefficient		Observed absorbance
Unsaturated carbonate	C_1	C=C	ε_1	D_1 (1660 cm^{-1})
		C=O	ε_2	D_2 (1760 cm^{-1})
6-Membered carbonate	C_2		ε_3	
5-Membered carbonate	C_3		ε_4	D_3 (1810 cm^{-1})

the molar concentrations of the three structural units can be expressed as;

$$C_1 = D_1/\varepsilon_1 l$$
$$C_2 = (D_2 - \varepsilon_2 D_1/\varepsilon_1)/\varepsilon_3 l$$
$$C_3 = D_3/\varepsilon_4 l$$

where l, denotes the thickness of a specimen. Assuming that the absorption coefficients of the three structural units can be represented by those of the corresponding model compounds in solution, the following expressions result:

$$C_1 = D_1/494l$$
$$C_2 = (D_2 - 2.97D_1)/1819l$$
$$C_3 = D_3/1960l$$

The relative amounts of C_1, C_2 and C_3 can be calculated independently of the thickness, l. The absorption bands at 1810 and 1760 cm^{-1} in the polymer, which overlapped each other, were separated as shown in Fig. 2. The 6-membered cyclic carbonate content was not determined directly, but it was calculated on the basis of the difference in the observed absorbance of unsaturated carbonate as calculated from the $\nu_{C=C}$ band at 1660 cm^{-1}. Therefore, its value is likely to have some error and to be less reliable. Cross-linking due to the pendant unsaturation may not be large, but its increase will result in the overestimation of the 6-membered carbonate in the above calculations. This is another source of error in the estimation of the 6-membered carbonate.

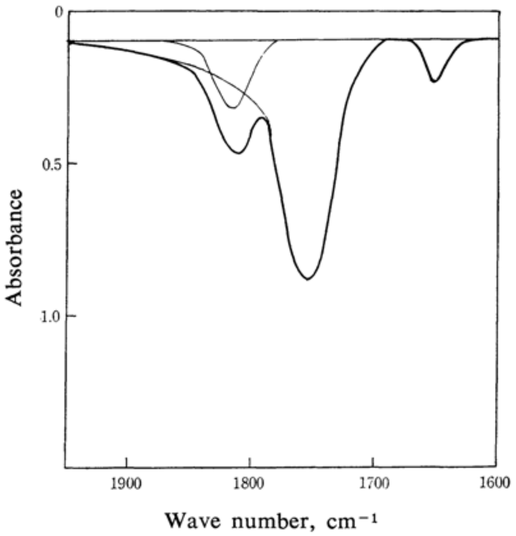


Fig. 2. Analysis of an infrared spectrum of polydivinyl carbonate.

The Effect of Polymerization Variables on Polymer Properties.—Gel point conversion may represent a qualitative measure of the degree of cyclization.[2] The effect of the monomer concentration on the gel point conversion is shown in Table II. When a visible gellation had taken place, almost the entire polymer was found to become insoluble; the monomer concentration in this case did not have any appreciable effect on the gel point conversion.

As it has been shown that, at a gel point conversion, almost the entire polymer becomes insoluble, the solubility of the polymers was examined at various points of conversion. The polymer was fractionated into a soluble part and an insoluble part by digesting the precipitated polymer with acetone at room temperature. The results are shown in Table III. The first appearance of gellation was observed after about 75 min. polymerization, but the insoluble

TABLE I. INFRARED ABSORPTION COEFFICIENTS OF THE RELATED MODEL COMPOUNDS

Carbonate	$\nu_{C=O}$, cm^{-1}	ε	$\nu_{C=C}$, cm^{-1}	ε
Divinyl carbonate	1775	1460	1660	752
Vinyl ethyl carbonate	1765	1470	1665	494
Diethyl carbonate	1745	1110		
2,3-Butanediol cyclic carbonate	1810	1960		
Propylene carbonate	1800	1490		
Trimethylene carbonate	1755	1970		
2,4-Pentanediol cyclic carbonate	1750	1810		
Poly(vinylene carbonate)[a]	1825			

a) H. C. Haas and N. W. Schuler, *J. Polymer Sci.*, **31**, 237 (1958).

TABLE II. POLYMERIZATION AND POLYMER STRUCTURE OF DIVINYL CARBONATE AT VARIOUS MONOMER CONCENTRATION IN BENZENE

60±0.05°C; [BPO]=0.5 mol. % of monomer

Exp. No.	1		2		3		4	
Monomer concn., % by Vol.	70		50		30		10	
Time, min.	52		77		112		1080	
Conversion, %[a]	12.2		13.9		11.1		14.7	
Sol. and insol. part, %	0.9	10.0	0.5	10.9	0.4	8.4	0.0	14.0
1,2-Addition, %	—	72	56	69	59	52	—	—
6-Membered ring, %	—	12	31	18	25	27	—	—
5-Membered ring, %	—	16	13	13	16	21	—	—

a) Polymerization was stopped at the first appearance of gellation except for No. 5 where no visible gellation was observed.

TABLE III. PROPERTIES OF POLYMERS OBTAINED AT VARIOUS CONVERSIONS

[M]=30 vol. % in benzene; [AIBN]=0.5 mol. % of monomer; 60±0.05°C

Exp. No.	5		6		7		8		9	
Time, min.	30		60		90		120		180	
Conversion, %	5.8		8.5		11.6		14.0		20.5	
Sol. and insol. part, %	5.3	0.0	3.7	4.7	1.3	9.5	1.1	12.1	0.5	20.0
1,2-Addition, %	—	—	59	52	—	—	48	51	59	48
6-Membered ring, %	—	—	25	27	—	—	36	31	21	33
5-Membered ring, %	—	—	16	21	—	—	16	19	20	19

Intrinsic viscosity of the soluble part of Nos. 5 and 6 are 0.109 and 0.118 dl./g. in acetone.

TABLE IV. EFFECT OF SOLVENTS ON POLYMERIZATION OF DIVINYL CARBONATE

[M]=30 vol. %, [AIBM]=0.5 mol. % of monomer; 60±0.05°C

Exp. No.	10		11		12		13		14		15	
Solvent	Benzene		Toluene		Cumene		CCl_4		Aceto-nitrile		Nitro-benzene	
Time, min.[a]	75		140		No gel.		135		140		No gel.	
Conversion, %	20.1		20.1		7		(70.1)[b]		25.6		0	
Sol. and insol. part, %	0.5	20.0	1.5	15.3	7	0	(21.0)	(48.6)	5.5	19.6	0	
1,2-Addition, %	59	52	61	60	61	—	91	52	40	48	—	—
6-Membered ring, %	25	27	21	21	26	—	0	29	21	19	—	—
5-Membered ring, %	16	21	18	19	14	—	9	19	39	33	—	—

Intrinsic viscosity of the soluble part of Nos. 12 and 14 are 0.062 and 0.080 dl./g. in acetone.

a) Time at the first appearance of gellation.

b) Cl%=19.76. Figures in parentheses are values corrected for chlorine, assuming that CCl_4 was incorporated by a chain transfer reaction.

TABLE V. BULK POLYMERIZATION OF DIVINYL CARBONATE AT VARIOUS TEMPERATURES

Monomer, 2 ml.; AIBN 0.1 mmol.

Exp. No.	1	2[a]	3	4[a]	5[a]	6[a]
Temperature, °C[c]	60	45	30	15	0	−30
Time, min.	14	3	1215	70	25	105
Conversion, %[b]	9.9	4.1	5.7	7.5	8.2	0.5
1,2-Addition, %	71	90	76	88	86	85
6-Membered ring, %	21	5.5	22	11	14	15
5-Membered ring, %	7.9	4.0	2.3	1.2	0.5	0

a) Photo-sensitized polymerization.

b) Polymerization was stopped shortly after gellation except for No. 6.

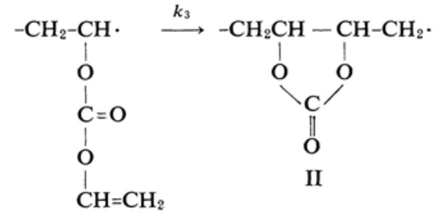
c) Temperature was kept constant within ±0.5°C.

polymer had been formed prior to the apparent gellation. At a conversion as low as 6%, the polymer was soluble in acetone, and thereafter the fraction of the insoluble polymer increased rapidly with conversion. The soluble part softened at 250—270°C with a slight discoloring. The polymer structure did not show appreciable change during the course of polymerization.

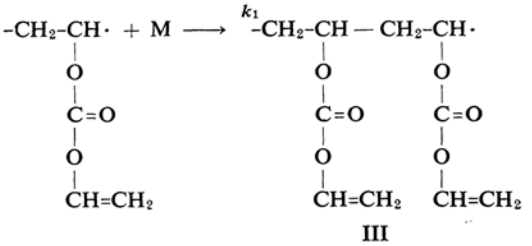
The solvent was expected to influence the solubility and the structure of the resulting polymer because of the differences in the chain transfer reaction and in the polarity, the latter of which might have some special influence on the conformation of the monomer molecule and of the polymer end in solution. The results are listed in Table IV. Even carbon tetrachloride, which is known to have a large chain transfer constant in the vinyl acetate polymerization, could not prevent the gel formation. However, polymerization in acetonitrile gave a polymer of a relatively high solubility. The extraordinary high yield of the polymer in carbon tetrachloride was unexpected: the reason can not be determined at present. Hydrocarbon solvents with high chain transfer constants, such as toluene and cumene, did not have any effect on the polymer structure, but a polar solvent, acetonitrile, showed such an effect, increasing the relative content of the 5-membered cyclic carbonate structure.

The Effect of the Polymerization Temperature on the Polymer Structure.—The formation of the 5-membered cyclic structure means the head-to-head addition of two vinyl groups in the same molecule. Head-to-head addition in usual vinyl monomers is known to have a higher activation energy than that of head-to-tail addition, and so it is to be expected that the polymerization temperature will have an effect on the content of cyclic units. The results are shown in Tables V and VI. The ratios of C_3/C_1, that is, the mole ratio of the 5-membered cyclic unit to the unsaturated carbonate units, is taken in an Arrhenius plot, giving the difference in the activation energies (Fig. 3):

$$E_3-E_1=6.21\pm0.29\ \text{kcal./mol. in a 50\% benzene solution}$$
$$=8.44\pm0.48\ \text{kcal./mol. in bulk polymerization}$$



II



III

Since

$$\frac{k_3}{k_1}=\frac{1}{(\mathrm{M})}\times\frac{A_3}{A_1}\exp\left(-\frac{E_3-E_1}{RT}\right)$$

Where (M) represents the monomer concentration in terms of the vinyl group, it follows

TABLE VI. PHOTOSENSITIZED POLYMERIZATION OF DIVINYL CARBONATE AT VARIOUS TEMPERATURE IN BENZENE (1 : 1 vol.)

Monomer, 2 ml.; Benzene 2 ml.; AIBM 0.1 mmol.

Exp. No.	7	8	9	10
Temperature, °C[a]	40	30	20	10
Time, min.	40	48	60	85
Conversion, %[b]	13.6	12.0	13.0	14.5
1,2-Addition, %	68	71	71	81
6-Membered ring, %	25	24	25	16
5-Membered ring, %	7.7	5.1	4.1	3.0

a) Temperature was kept constant within ±0.1°C.

b) Polymerization was stopped shortly after gellation.

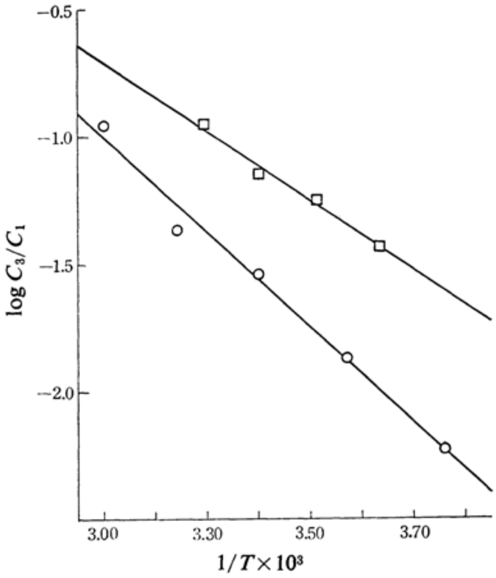


Fig. 3. Dependency of relative abundance of 5-membered ring on temperature of polymerization.

☐ Solution polymerization in benzene (50 vol. %)

○ Bulk polymerization

that;

$A_3/A_1 = 2.04 \times 10^4$ in a 50% benzene solution
$= 5.85 \times 10^5$ in bulk polymerization

Discussion

The experimental facts concerning the polymerization of divinyl carbonate at low conversions may be summarized thus:

i) The polymer structure has been found to be composed of a 5-membered cyclic carbonate unit, a 6-membered cyclic carbonate unit, and an unsaturated carbonate unit.

ii) Cyclopolymerization is not a predominant mode of propagation, leaving not less than half a mole of unsaturation per unit structure. Hence, the polymers are likely to be cross-linked.

iii) The polymerization variables, i. e., the concentrations of the monomer, the conversion, and the solvent, had no appreciable effect on the polymer structure except for the polymerization in acetonitrile (Table IV).

iv) The polymerization temperature had a strong influence on the polymer structure, raising temperature resulting in an increased content of the 5-membered cyclic carbonate unit.

Divinyl compounds which undergo cyclopolymerization may be classified into two types. The one is compounds with unsaturated groups relatively inactive towards a radical, such as diallyl compounds and divinyl acetals. The other one is monomers with the reactive double bonds, like acrylic anhydride and its derivatives. Recently, it has been suggested, from a study of the electronic spectra, that two double bonds in a molecule of the latter type have a mutual interaction in solution and that the molecule takes a special conformation favorable to cyclization.⁶⁾ The vinyl groups in divinyl carbonate belong to the latter type, its reactivity is not very different from that of vinyl acetate.⁷⁾ The fact that divinyl carbonate is unlikely to undergo genuine cyclopolymerization might be due to the lack of a conformation favorable to cyclopolymerization in this case.

Gellation at the stage of low conversion is explained as being due simply to the prior existence of a large amount of the pendant vinyl groups in the polymer and to the high reactivity of the vinyl group.

The temperature dependency of the polymer structure is significant. The intramolecular formation of the 5-membered cyclic unit has a larger activation energy, from 6 to 8 kcal./mol., than the intermolecular propagation. The difference in the activation energies between the head-to-head addition and the head-to-tail addition of the usual monomers is reported to be 1 to 3 kcal./mol.⁸⁾ The formation of the 5-membered cyclic unit of divinyl carbonate implies an intramolecular cyclization as well as a head-to-head addition. Therefore, the cyclization reaction may need an additional activation energy to be able to take a conformation favorable to the ring closure.

The frequency factor of the 5-membered cyclization reaction (A_3) is larger than that of the intermolecular propagation (A_1) by a magnitude of 10^4 to 10^5. The ratios observed in other vinyl monomers range from 0.1 to 0.7.⁸⁾ This large difference may not be unreasonable when it is considered that the reacting vinyl group in the cyclization reaction always exists in the vicinity of the reacting polymer radical. In other words, the intramolecular cyclization needs less decrease of entropy at the activated state than does the intermolecular propagation.

Summary

The preparation of divinyl carbonate has been described. The cyclopolymerization of the monomer has been studied under various reaction conditions, and it has been found that cyclopolymerization is not a predominant mode of propagation, for it leaves not less than half a mole of unsafuration per unit structure. The polymer structure has been analyzed by the infrared method and found to contain the 5-membered cyclic carbonate unit, the 6-membered cyclic carbonate unit and the pendant unsaturated carbonate unit.

The polymerization temperature has been shown to have a significant effect on the 5-membered cyclic unit content, increasing the temperature resulting in an increase in the 5-membered unit. The activation energy difference between the intramolecular 5-membered cyclization and the intermolecular propagation has been estimated to be 6.21±0.29 kcal./mol. in the polymerization in a 50% benzene solution and 8.44±0.48 kcal./mol. in bulk polymerization.

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6) G. B. Butler and J. W. Brooks, *J. Org. Chem.*, **28**, 2699 (1963).

7) S. Murahashi, S. Nozakura and K. Kikukawa, to be published.

8) I. Rosen, G. H. McCain, A. L. Endrey and C. L. Sturm, *J. Polymer Sci.*, **A1**, 951 (1963).