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POLY(VINYL ALCOHOL)-IODINE REACTION

CONTENTS

Poly(vinyl alcohol)-Iodine Reaction

Introduction

Since the blue color reaction of poly(vinyl alcohol)(PVA) with iodine was observed by Herrmann et al.[1)] and staudinger et al.[2)] as early as 1927, numerous investigators have demonstrated the effects of the reaction conditions and the structure of PVA on this reaction.

Effect of the reaction conditions was studied systematically in detail by Zwick[3)] and a helical structure of the PVA-iodine complex was proposed.Hayashi et al. noted that the dilute aqueous solution of partially saponified poly(vinyl acetate)(PVAc) colored red by treating with iodine as PVAc did, but that of partially acetylated PVA did not turn red with iodine, even if both were equal in the average degree of acetylation[4)]. Imai et al. reported that the PVA-iodine reaction is sensitive to molecular weight and stereoregularity[5)]. Longer and more syndiotactic PVA display higher color intensities under the same conditions than polymers with shorter chains and more random molecular configuration. A quantitative relationship was establised between molecular weight and the color intensity of the PVA-iodine reaction and the more syndiotactic polymer reported to exhibit more intensive color.

Onthe other hand, it has been known that the variation at the molecular fine structure of PVA influences the properties of PVA. For example, Murahashi et al. noted that isotacticity and the 1,2-glycol structure lower the melting point and deteriorate the crystallinit[6,7].

Imai et al. separated a PVA derived from PVAc into fractions by foaming an aqueous solution[8]. Fractions showed different reactivity to the PVA-iodine reaction inspite of little difference of degree of polymerization and 1,2/glycol content. They have suggested that the PVA have been separated according the stereoregularity.

This work was undertaken to study the effect of the structural variations on the PVA-iodine reaction and to make an approach to the elucidation of the structure of the PVA-iodine complex.

Chapter I describe the preparation of atactic PVA having various amount of the 1,2-glycol structure, in other words head-to-head, starting from a new monomer, divinyl carbonate. Further study was made on the cyclopolymerization of homologous divinyl esters in the hope of synthesizing PVA rich in the 1,2-glycol structure. Divinyl carbonate was found to the most suitable monomer for this purpose. In addition copolymerization parameters of divinyl carbonate were determined.

Effect of the 1,2-glycol structure and stereoregularity on the PVA-iodine reactions was studied in Chapter II. The presence of the 1,2-glycol structure in atactic PVA did not change the structure of the complex but decreased the concentration of the complex, whereas isotacticity not only decreased the concentration but also modified the structure of the complex. The shortest sequence which is needed for the complex formation was estimated to be 120 monomeric unit of the atactic structure.

In Chapter III foam fractionation of aqueous PVA solution were carried out according to Imai et al.8) It was confirmed that the intensity of the PVA-iodine color reaction decrease with the increase of the fraction numbers. The origin of this difference was pursued from the view point of structural variations such as molecular weight, stereoregularity, the 1,2-glycol content, and the carbonyl content but none of these factors could elucidate the difference. Short branching was suggested as a probable factor which will influence the iodine-color reaction as well as the foam fractionation.

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Chapter I

Preparation of Poly(vinyl alcohol) Containing Various of the 1,2-Glycol Structure via Cyclopolymerization of Divinyl Esters of Dibasic Acids.

I-1

Preparation and Polymerization of Divinyl Carbonate

Synopsis

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 unsaturation 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+0.29kcal/mol in the polymerization in a 50% benzene solution and 8.44+0.48kcal/mol in bulk polymerization.

The Preparation and Polymerization of Divinyl Carbonate*

By Shunsuke MURAHASHI, Shun'ichi NOZAKURA, Saburo FUJI
and Kiyoshi KIKUKAWA

(Received March 15, 1965)

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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* Part of this paper was presented at the 17th Annual Meeting of the Chemical Society of Japan, April, 1964.

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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:

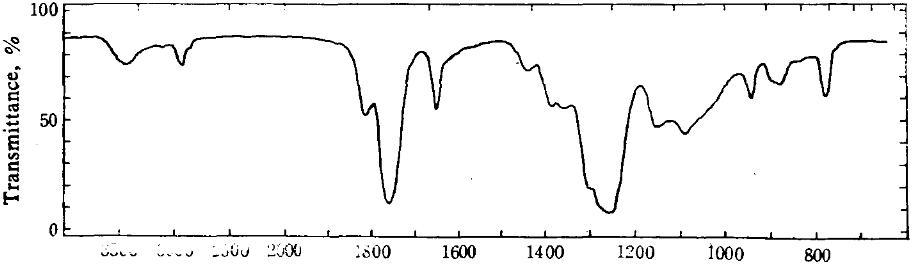
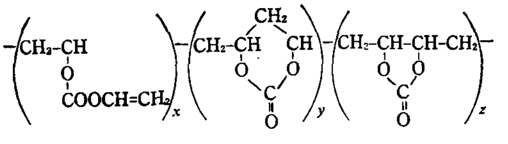


Fig. 1. Infrared spectrum of polydivinylcarbonate.



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.

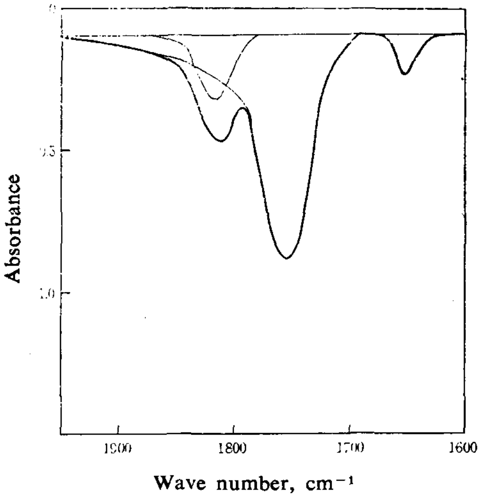


Fig. 2. Analysis of an infrared spectrum of polydivinyl carbonate.

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.

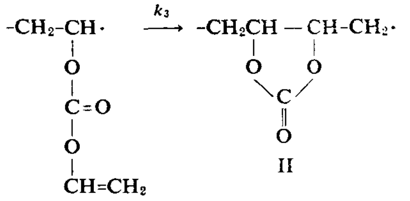
polymer had been formed prior to the apparent gellation. At a conversion as low as 6%, the polymer was soluble in acetone, and thereafter the fraction of the insoluble polymer increased rapidly with conversion. The soluble part softened at 250—270°C with a slight discoloring. The polymer structure did 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):

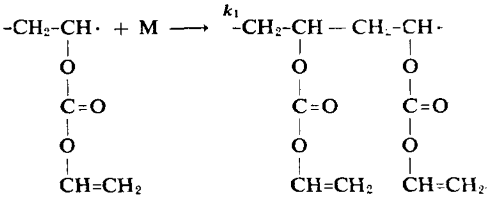
$$E_3-E_1=6.21\pm0.29\ \text{kcal./mol. in a 50\% benzene solution}$$

$$=8.44\pm0.48\ \text{kcal./mol. in bulk polymerization}$$



$$-CH_2\text{-}CH(OCOOCH{=}CH_2)\cdot \xrightarrow{k_3} -CH_2CH-CH\text{-}CH_2\cdot\ (\text{cyclic } -O-C(=O)-O-)$$

II



$$-CH_2\text{-}CH(OCOOCH{=}CH_2)\cdot + M \xrightarrow{k_1} -CH_2\text{-}CH(OCOOCH{=}CH_2)-CH_2\text{-}CH(OCOOCH{=}CH_2)\cdot$$

III

Since

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

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.

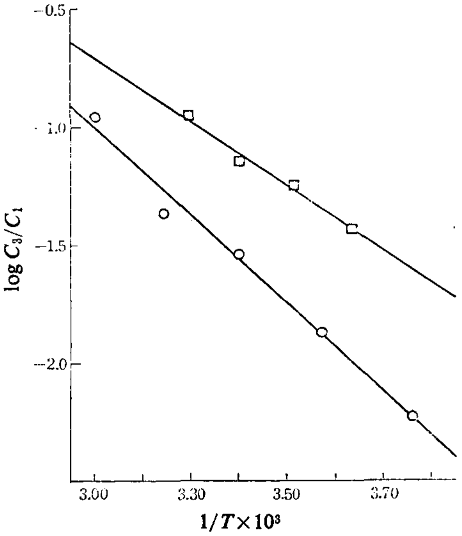


Fig. 3. Dependency of relative abundance of 5-membered ring on temperature of polymerization.

☐ Solution polymerization in benzene (50 vol. %)

○ Bulk polymerization

that;

$A_3/A_1=2.04\times10^4$ in a 50% benzene solution

$=5.85\times10^5$ 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 crosslinked.

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 unsaturation 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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I-2

Structure of Poly(vinyl alcohol) derived from Polymers of Divinyl Carbonate

Synopsis

The structure of poly(vinyl alcohol) derived from poly(divinyl carbonate) or divinyl carbonate-vinyl acetate copolymers was studied. These poly(vinyl alcohol) were found to contain an unusually large amount of 1,2/glycol structure, which is considered to due to the 5-membered ring structure in poly(divinyl carbonate) or divinyl carbonate-vinyl acetate copolymers. With increasing the 1,2-glycol structure in poly(vinyl alcohol)(3mol% - 45mol%), the melting points of poly(vinyl alcohol) decreased and the infrared absorption of C-O stretching mode shifted from $1090cm^{-1}$ to $1050cm^{-1}$. The melting behavior in diffrential thermal analysis was not observed in poly(vinyl alcohol) which contained the 1,2-glycol structure in more than 40mol%.

Variation of melting points with the contents of 1,2-glycol structure was interpreted by the Flory's theory, giving 1.67kcal/mol for the heat of fusion of poly(vinyl alcohol) and 243°C for the melting point of pure poly(vinyl alcohol).

〔5〕 炭酸ジビニルの重合体より得られるポリビニルアルコールの構造

（1967年6月27日受理）

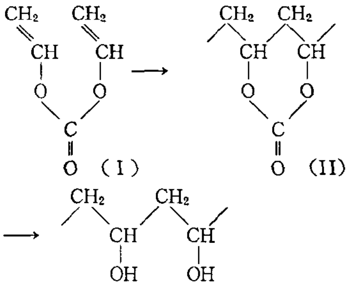
菊川　清*・野桜俊一*・村橋俊介*

要　旨　ポリ炭酸ジビニル（PDVC）あるいは炭酸ジビニル－酢酸ビニル共重合体（DVC-VAc）より得られるポリビニルアルコール（PVA）の構造について検討した。これらの PVA は PDVC および DVC-VAc 共重合体中の5員環構造に由来する多量の1，2-グリコール構造を含んでいる。1，2-グリコール構造が増加するに従い（3 mol %～45 mol %），PVA の融点は低下し，赤外吸収スペクトルの C-O 伸縮振動も 1090 cm^{-1} から 1050 cm^{-1} へ移動する。1，2-グリコール構造を 40 mol % 以上含む PVA では，示差熱分析で融点が認められなかった。1，2-グリコール量による融点の変化を Flory の理論により取り扱い，PVA の融解熱として 1.67 kcal/mol を得た。また，1，3-グリコールだけからなり 1，2-グリコール構造を含まない PVA の融点として 243°C を得た。

1. 緒　　言

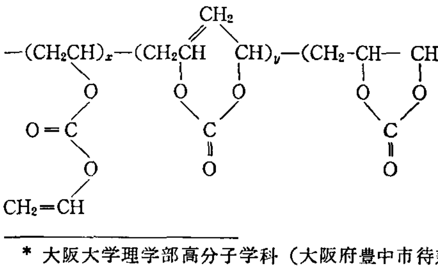
Butler ら[1]によりジビニル化合物の分子内-分子間重合が見出されて以来，多くのジビニル化合物が環化重合を行ない，可溶性ポリマーを生成することが報告されている。

炭酸ジビニル（DVC）も同様な環化重合により，（I）式の（II）の構造をもつポリマーの生成が予想される。またポリマーの加水分解が行なわれればポリビニルアルコール（PVA）が得られるはずであり，環化重合により特異な立体構造をもった PVA が得られる可能性がある。



（1）

このような観点から，以前にわれわれは DVC の単独重合を行ない，そのポリマーが（2）式に示したような構造をもつことをその IR スペクトルから推定した。



（2）

さらに，その構造単位に及ぼす重合条件の影響を検討した[2]。その結果，重合率，溶媒によっては大きな影響は受けないが，重合温度により大きな影響が認められた。

本報においては，ポリ炭酸ジビニル（PDVC）の加水分解が比較的容易に行なえることを見出したので，PVA としての構造の特異性を検討した。さらに前報においては PDVC 中の5員環構造の定量を，IR スペクトルにより，モデル物質の吸光係数を用いる仮定に基いて行なったので，加水分解して得られる PVA の1，2-グリコール構造の定量により，もとの5員環構造の直接的確認を行なうことも一つの目的とした。

2. 実　　験

2.1 モノマー，溶媒

DVC は前報に記したように，ホスゲンと $Hg(CH_2CHO)_2$ より合成した[2]。bp 44.7～45.3°C/85 mmHg。

酢酸ビニル（VAc）は重亜硫酸ソーダ水溶液で洗い，$CaCl_2$ で乾燥した後，蒸留して用いた。2，2′-アゾビスイソブチロニトリル（AIBN）は市販品を EtOH より再結晶して用いた。

2.2 重　合

Expt. No. 1～10 は，前報[2]において，塊状および 50 vol % ベンゼン溶液で，重合温度を変化させて得たポリマーである。低温においては紫外線による光増感重合を行なった。その他はすべて，モノマー，溶媒および開始剤を入れたガラスアンプルを，真空系で3回脱気後，封管して 60°C の恒温槽で静置重合した。重合終了後ゲルを含む溶液を多量の石油エーテル中へ注ぎ，ポリマーを沈殿させ，数回のデカンテーションをくり返したのち，室温で減圧乾燥した。重合は単独重合で 10～15 %，共重合で 15～25 % の重合率とした。すべての系で，ポリマーの沈殿（ゲル）が生ずる。

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2.3 ポリマーの加水分解

200ccの三角フラスコに0.2〜0.4gのポリマーをとり，アセトン50ccを加え十分膨潤させる（4〜5時間）。そこへ1N-KOH水溶液10ccを加える。このときポリマーのほとんどが溶解する。このまま室温で2〜3日放置すると完全に加水分解され，試料No. 1〜10の場合ではPVAが沈殿してくる。その他の試料の場合には下層に溶解している。これを多量のメタノールに注ぎ，ポリマーを沈殿させる。デカンテーションをくり返したのち，遠心分離して（試料No. 1〜10ではグラスフィルターでロ別した），メタノールで洗浄し，室温で減圧乾燥した。

2.4 1，2-グリコール構造の定量

過ヨウ素酸（HIO_4）法によった。本報では主として，浮田らの方法により[3]ポーラログラフ法でHIO_4を定量した。波高としては電解回路を切ったときの値を0点とし，−0.1V（SCE）における電流値を拡散電流として用いた。PVA濃度の影響を調べた結果，その濃度が0.045〜0.075％の範囲ではその波高に大きな影響は認められなかった。そこで，約0.06％の水溶液として測定した。

また，PVA濃度0.052％において，HIO_4濃度と波高との比例性を検討した結果，HIO_4濃度が0〜16m mol/lの範囲ではTable 1に見られるように良好な比例関係が認められた。

なお比較のため，Expt. No. 24〜29の試料についてはH.E. Harrisらの方法[4]により，反応後のHIO_4を定量して，1，2-グリコール量を求めた。

2.5 IRスペクトル

約1％水溶液よりフィルムを作成して，日立分光光度計EPI＝2型により測定した。

2.6 PVAの重合度

1％水溶液の粘度から中島の式[5]を用いて求めた。

2.7 PVAの融点測定

Sample No. 24〜27については，倉敷レイヨン株式会社研究所において，島津示差熱分析計DT-10型を用いて測定した。No. 28, 29については，ニチボー株式会社繊維研究所において，島津示差熱分析計DT－10型を用いて測定した（Fig. 2）。

Table 1. The proportionality between HIO_4 concentration and diffusion current.
[PVA]＝0.052％ at 25°C

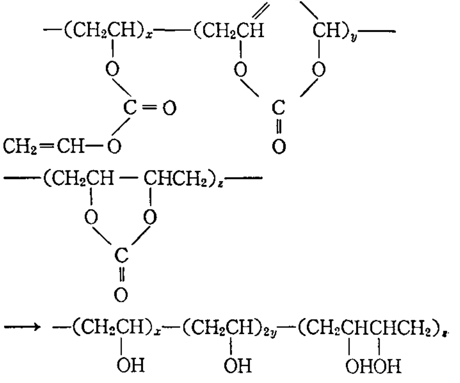
[HIO_4] (m mol/l)	i_d (μA)	i_d/C
0.0	0	—
0.4	1.72	4.27
0.8	3.42	4.27
1.2	5.19	4.32
1.6	6.48	4.27

3. 結　　果

3.1 PVAの1，2-グリコール構造について

前報[2]において，重合温度を変化させて得られたPDVCを加水分解して得られたPVAの1,2-グリコール量のHIO_4酸化法による測定値をTable 2に示した。Table 2にはIRスペクトルによる5員環構造の定量値より計算した1，2-グリコール量も示した。5員環構造に由来する1,2-グリコール構造のmol％は，（3）式により，

$\{2z/(x+2y+2z)\}\times100$ として計算した。



（3）

すなわち，Table 2の1，2-グリコールmol％は，一般に用いられている100⊿（100個のモノマー単位の中に含まれる1，2-グリコール構造の数）の値の2倍に相当する。

HIO_4酸化法により求めた1，2-グリコール量と，IRスペクトル法より求めたそれとが，5員環量の少ない範囲（＜15％）において，かなりよい一致を示すことがわかった。モデル化合物としてのエチルビニル炭酸の単独重合体より得られたPVAについてもTable 2に示したが（Sample No. 284），その1，2-グリコール量はポリ酢酸ビニルよりのPVAよりやや多い程度である。

3.2 1，2-グリコール量の変化によるPVAのIRスペクトルおよび融点の変化

DVCはVAcとよく似た重合反応性を示すことがわかったので[6]，DVCとVAcの共重合を行ない，その共重合体を加水分解すれば，1,2-グリコール量の変化したPVAを得ることが予想される。

1，2-グリコール量の変化によるIRスペクトル，および融点（T_m）の変化を調べるために，DVC-VAcの共重合を行った結果をTable 3に示した。またPVAのIRスペクトルをFig. 1に示した。PVAのシンジオタク

Table 2. 1, 2-glycol contents of PVA derived from polydivinylcarbonate.

Sample No.	[M] (vol %)	Polymerization temp. (°C)	1, 2-glycol contents (mol %)		$\frac{D_{916}}{D_{849}}$	$\overline{DP}$
			obsd.	calcd. from IR		
1	100	60	13.7	12.2	0.30	631
2	(bulk)	45	9.6	7.3	0.37	—
3		30	6.4	3.7	0.40	—
4		15	4.7	2.1	0.43	—
5		0	3.5	0.9	0.45	—
7	50	40	10.8	11.5	0.34	593
8		30	7.6	7.9	0.33	610
9		20	5.7	6.3	0.26	606
10		10	6.7	5.0	0.33	623
23	11.4	60	30.0	42.8	0.18	—
284*	bulk	60	4.7	—	0.23	196
Commercial PVA			3.3			500

* Sample No. 284 was derived from polyethylvinylcarbonate.

Table 3. The IR spectra, melting points and 1, 2-glycol contents of PVA derived from DVC-VAc copolymers and PDVC.

Expt. No.	DVC, mol % in monomer	DVC, mol % in polymer	1, 2-glycol (mol %)	$\frac{D_{916}}{D_{849}}$	ν_{C-O} (cm^{-1})	$\overline{DP}$	T_m (°C)
20	20.0	27.2	11.4	0.30	1090	358	—
21	50.0	55.5	19.7	0.25	1075	—	—
22	80.0	84.1	24.0	0.25	1060	274	—
23	100	100	30.0	0.18	1060	—	—
24	25.0	—	12.1	0.24	1090	243	207
25	50.0	—	19.5	0.21	1075	237	181
26	75.0	—	25.6	0.22	1060	—	164
27	100	—	—	0.18	1060	—	118
28	100	—	42.0	0.19	1050	188	decomp.
29	100	—	45.8	0.17	1050	164	decomp.

Conditions for polymerization in benzene at 60°C,
No. 20〜27: [DVC]+[VAc]=2mol/l, [AIBN]=0.0134mol/l,
No. 28: [DVC]=10vol%, [AIBN]=0.075mol/l
No. 29: [DVC]=5vol%, [AIBN]=0.038mol/l

トの指標とされている7) IR スペクトルの吸光度比 D_{916}/D_{849} の値が，1,2-グリコール量の増加により減少する傾向にある。さらにC-O伸縮の振動とされている1090cm^{-1}の吸収が 1050cm^{-1}へ移動することが認められた。さらに 1, 2-グリコール量の増加は著しく融点を低下させ，Expt. No. 28, 29 では，はっきりした融点は認められなかった。Fig. 2 に示差熱分析の結果を示す。

4. 考　　察

Table 2 に見られるように，過ヨウ素酸酸化法による 1, 2-グリコール量と，IR スペクトル法によるそれとが 5 員環量の少ない範囲（<15%）でかなりよい一致を示している。モデル化合物と考えられるポリエチルビニル炭酸より得られた PVA の 1, 2-グリコール量（4.7mol%）は市販 PVA のそれ（3〜4mol%）より少し多い程

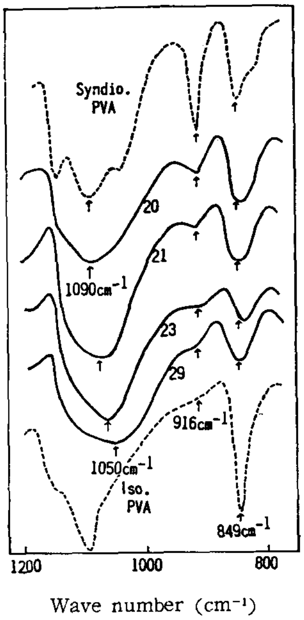


Fig. 1. IR Spectra of PVA containing the 1, 2-glycol structure

度である。すなわち，1，2-グリコールが主として5員環構造に由来していると思われる。これより，PDVC中の5員環構造の定量に IR スペクトルを用いることは，少なくとも5員環構造のそれほど多くないときには妥当であろう。5員環構造の多い場合にずれの大きいことは，PDVC の IR スペクトル中での5員環構造に由来する $\nu_{C=O}$ の $1815\,\mathrm{cm}^{-1}$ の吸収と6員環およびペンダントカルボナート構造に由来する $\nu_{C=O}$ の $1760\,\mathrm{cm}^{-1}$ の吸収との重なりが大きいために，IR スペクトル法において誤差が大きいと考えられる。

Table 3 に見られるように，1，2-グリコール量の変化により，PVA の IR スペクトル，およびその融点に大きな変化が認められる。

まず，シンジオタクトの指標とされている，IR スペクトルの吸光度比 D_{916}/D_{849} の値が，1，2-グリコール量の増加により減少する傾向が見られる。これは Fig. 1 に同時に示した典型的なイソタクト PVA およびシンジオタクト PVAの吸収と比べてみると，特に$849\,\mathrm{cm}^{-1}$の吸収はイソタクト PVA とは大きな差があり，D_{916}/D_{849} の値の減少がイソタクト構造の増加とは考えにくい。849 cm^{-1} の吸収の形はむしろシンジオタクト PVA のそれに近い。さらに Fig. 1 にあげたシンジオタクト PVA が，その PVAc 誘導体の NMR スペクトルにより，ヘテロタクト構造を多く含んでいること（I 6, H 40, S 54）[8] を考えあわせると，$849\mathrm{cm}^{-1}$ の幅広い吸収はヘテロタクト構造に帰因することが予想される。この点に関しては，さらに検討が必要であろう。

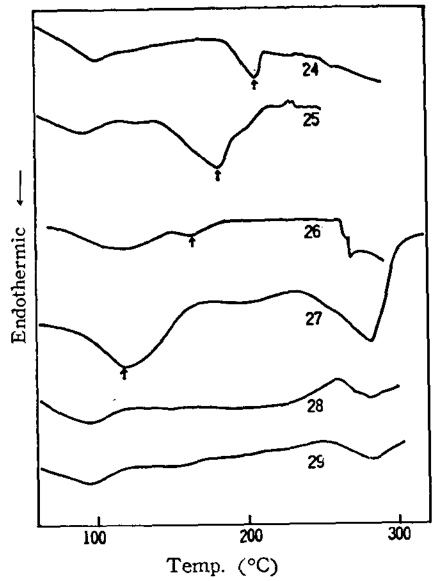


Fig. 2. Thermograms of PVA.

次に，ν_{C-O} の吸収と考えられる $1090\mathrm{cm}^{-1}$ の吸収が，1,2-グリコール量の増加とともに $1050\,\mathrm{cm}^{-1}$ へ移動していることが特徴的である。このことは一般に第2級アルコールの ν_{C-O} がその α 炭素（$-\overset{\alpha}{\underset{|}{\mathrm{C}}}-\mathrm{CHOH}$）に枝分れがあるとき約 $10\sim15\,\mathrm{cm}^{-1}$ 低波数側へ移動することが知られていること[9] から，理解されよう。また，この深色移動が，1，2-グリコール量が 20 mol％を越えるころから始まることは興味深い。

1，2-グリコール量が増加するに従い，PVA の融点が顕著に低下している。これは PVA 中に異種結合である1，2-グリコール構造が入ることにより結晶化を妨げていると考えられる。このことはまた，Fig. 1 に見られるように，IR スペクトルで結晶化バンドとされている $1140\,\mathrm{cm}^{-1}$ の吸収が，Expt. No. 20 でわずかに肩が認められる程度で，ほとんど消失していることからも推察される。

Flory[10] は結晶化するA単位と結晶化しないB単位との共重合体において，次の式に従って，B単位がA単位の融点を低下させることを示している。

$$\frac{1}{T_m}-\frac{1}{T_m{}^0}=-\left(\frac{R}{\Delta H_u}\right)\ln N_A \qquad (4)$$

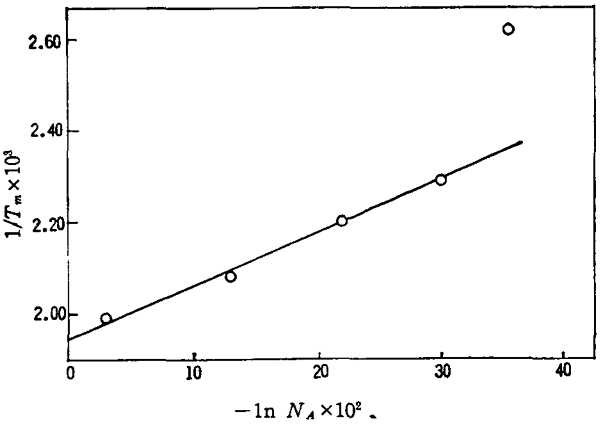


Fig. 3. Melting points of PVA plotted according to eq. (4).

ここで，N_A はA単位のモル分率，T_m^0 はA単位のポリマーの融点，ΔH_u は融解熱である。

今，1,2-グリコール構造を1,3-グリコール構造からなるPVA中に入った結晶化を乱す共重合物と考えると，N_A は PVA 中の 1,3-グリコール構造のモル分率であり，$1/T_m$ と $-\ln N_A$ をプロットすれば直線となるはずである。このプロットを Fig. 3 に示した。右端の点 (Expt. No. 27) を除いて，かなりよい直線関係があることがわかる。Expt. No. 27 の点が直線よりずれている原因としては，一つには，この融点が，Fig. 2 にみられるようにポリマー中に含まれている水の影響を受けており，その値に大きな信頼をおけないためとも考えられる。また，1,2-グリコールのさらに多い Expt. No. 28, 29 では，はっきりした融点を認めることができないことを考えあわせると，1,2-グルコール構造が 30% 付近以上では，ポリマーの結晶化に必要な 1,3-グリコール連鎖の長さに不足してきて，結晶化部分が急激に減少してきたためとも考えられる。この点に関しては，さらに他の方面からの検討が必要であろう。

Fig. 3 の直線部分の勾配から，融解熱 ΔH_u ($-CH_2CHOH-$単位あたり) を求めると 1.67 kcal/mol となり Tubbs[11]が，PVA をグリセロールに稀釈して求めた値 1.64kcal/mol とよい一致を示す。また，直線のたて軸に対する切片から，1,2-グリコールを含まない PVA の融点 T_m^0 として 243°C が求められる。3～4 mol % の 1,2-グリコールを含む市販 PVA の融点は 230°C であり，上記の値は妥当であろう。

以上みてきた結果から，1,2-グリコール構造の存在は PVA の結晶化に大きな影響を与えており，その少ない範囲では ($\lesssim$25 mol %)，その増加に比例して結晶化部分を減少させると考えられる。また 1,2-グリコール量が 40 mol % を越えると無定形ポリマーを与える。

付 記：示差熱分析をお願いした，倉敷レイヨン株式会社研究所長，松本昌一博士，ニチボー繊維研究所長，木津英雄博士，ポーラログラフの測定について指導していただいた，大阪大学理学部池田重良教授，種々の助言をしていただいた，鷲見正雄博士に深く感謝の意を表します。

なお，内容の一部は，第12回高分子研究発表会（1966年，神戸）で発表した。

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I-3

Cyclopolymerization of Divinyl Esters of Dibasic Acids and Structure of Poly(vinyl alcohol) derived from the Polymers

Synopsis

Divinyl esters of dibasic acids($CH_2=CHOCO(CH_2)_{n-3}COOCH=CH_2$, n=2 - 10) were synthesized and polymerized with radical initiator, and the structure of poly(vinyl alcohol) derived from the polymers were studied. The cyclopolymerizability of these monomers was nearly equall or less than that of divinyl carbonate which was previously reported, and the extent of cyclization was 15% - 65%. All the monomers yielded gelled polymers. The monomers which are to yield even membered rings tend to cyclopolymerized easier than odd membered rings. Poly(vinyl alcohol) derived from these polymers showed similar structure with respect to 1,2-glycol content and stereoregularity to that from poly(vinyl acetate).

Introduction

We have previously studied the cyclopolymerizability of divinyl carbonate and the properties of the poly(vinyl alcohol) (PVA) derived from its polymer, and have shown that divinyl carbonate is cyclopolymerized with a radical initiator to give the polymer containing the 5-membered ring in part(~30mol%), that is, the head-to-head type cyclopolymerization occurs1,2). Therefore, PVA derived from poly(divinyl carbonate) by saponification contains a large amount of the 1,2-glycol structure (~40mol%) and exhibits different properties from that derived from poly(vinyl acetate). For example, the increase of the 1,2-glycol structure lowers the melting point of PVA and deteriorates the crystallinity2). Furthermore the 1,2-glycol structure affects violently the PVA-iodine blue color reaction3,4). It is therefore, of interest to prepare the PVA containing a large amount of the 1,2-glycol structure and to study its properties. For this purpose, divinyl esters of dibasic acids other than divinyl carbonate were studied.

The 5-membered ring structure is formed as well as the 6-membered ring in the case of the polymerization od divinyl carbonate1), whereas the 7-membered ring structure is hardly formed compared with the 6-membered ring at the ring closure reaction of low molecular weight compounds5). Thus, divinyl oxalate may be a suitable monomer for the preparation of the head-to-head linkage in PVA; for the formation of the 6-membered ring(head-to-head) competes with that of the 7-membered ring(head-to-tail) In the cyclopolymerization of divinyl oxalate. If the 6-membered ring is formed predominantly, the derived PVA will mainly be comprized of the 1,2-glycol structure. Although Mark claimed such an idea for divinyl oxalate6), the structure of the polymer has not been reported in detail.

In the present paper we have dealt with the synthesis and the polymerization of the divinyl esters of dibasic acids, $CH_2=CHOCO(CH_2)_{n-3}COOCH=CH_2$, $n = 2 \sim 10$, and have studied their cyclopolymerizability and the property of the PVA derived from the polymers in comparison with the case of divinyl carbonate.

Experimental

Preparation of Monomers

Divinyl esters of oxalic, malonic and succinic acid were synthesized by a reaction of mercuridiacetaldehyde with the corresponding acid chlorides in ether similarly to the method for divinyl carbonate1). A typical reaction condition is described below.

A mixture of 120g of mercuridiacetaldehyde, 200ml of ether and a slight amount of hydroquinone was placed in a 500ml three-necked flask equipped with a reflux condenser with a calcium chloride tube, a stirrer and a dropping funnel, and the flask was cooled with an ice bath. A solution of 27g of oxalyl chloride in 45ml of ether was added to the flask with stirring during half an hour, and stirred for additional one hour at room temperature. The resulting chloromercuriacetaldehyde was removed by filtration and the filtrate was subjected to distillation at reduced pressure. The yield was 18.1g, 64% based on oxalyl chloride.

Divinyl esters of glutaric, adipic, pimelic, suberic, azeraic and sebacic acid were synthesized by the well-known transvinylation reaction of acid with an excess of vinyl acetate using mercuric acetate and sufuric acid as catalysts$^{7)}$. A typical reaction condition is described below.

A mixture of 30g of adipic acid, 200ml of vinyl acetate, 1g of mercuric acetate, 0.2ml of sulfuric acid and a slight amount of cupric stearate or copper powder was placed in a 500ml three-necked flask equipped with a reflux condenser with a calcium chloride tube and a mechanical stirrer, and the flask was heated to reflux the reaction mixture with an oil bath. After 10 hours 0.8g of sodium acetate was added to the cooled reaction mixture. The excess of vinyl acetate was evaporated by an aspirator at room temperature and the residual solution was distilled at reduced pressure. The yield was 26g, 64% based on adipic acid.

The results for all the divinyl esters were summerized in Table I. IR and NMR data are shown in Table II.

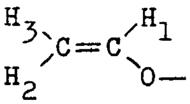
Other materials were purified in the usual way.

Table I. Syntheses of Divinyl Esters

Divinyl Esters	Yield %	b.p. °C/mmHG	m.p. °C	n_D^{25}	Found		Calcd.	
					C	H	C	H
Oxalate	64	81.8 ~82/45	23.0 ~23.5	1.4460	49.90	4.17	50.71	4.26
Malonate	42	65.3 ~65.5/6	-90 ~-100	1.4440	53.37	5.06	53.84	5.16
Succinate	68	50/3	25.0 ~25.5	1.4477	-	-	-	-
Glutarate	48	78 ~80/2	-	1.4488	58.25	6.50	58.68	6.57
Adipate	64	59 ~61/2	-	1.4480 (30°C)	-	-	-	-
Pimelate	60	107/1	-	1.-	62.29	7.57	62.25	7.60
Suberate	-	99/1	-	-	63.71	8.00	63.70	8.02
Azerate	75	110 ~114/1.5	-	-	64.76	8.33	64.98	8.39
Sebacate	66	141 ~145/3	7~8	1.4521	65.79	8.65	66.12	8.72

Table II. Spectroscopic Data of Divinyl Esters

Divinyl Esters	Infrared spectra, cm^{-1}		NMR spectra, τ, a)		
	$\nu_{c=o}$	$\nu_{c=c}$	H_1	H_2	H_3
Carbonate	1775	1660	2.85	5.00	5.35
Oxalate	1764 1790	1651	3.15	5.30	5.54
Malonate	1752 1770	1650	2.73	5.08	5.38
Succinate	1760	1650	2.71	5.12	5.38
Glutarate	1760	1650	2.72	5.17	5.43
Adipate	1760	1650	2.72	5.18	5.48
Pimelate	1763	1650	-	-	-
Suberate	1762	1650	-	-	-
Azerate	1763	1650	-	-	-
Sebacate	1760	1650	2.72	5.20	5.50

a) H_1, H_2 and H_3 represent vinylic proton, 

The esters were examined as 10vol% solutions in carbon tetrachloride and the chemical shifts were measured from tetramethylsilane internal reference.

Polymerization Procedure

An ampoule containing a monomer, benzene and 2,2′-azobisisobutyronitrile(AIBN) was degassed three times by the freeze-thaw method, and then sealed under vacuum($\sim 10^{-3}$mmHg). Polymerization was carried out in a thermostat at 60±0.005℃. The polymerization mixture, which almost gelled, was poured into a large amount of petroleum ether, yielding a precipitate of polymer. The polymer was washed several times with petroleum ether by decantation and separated by centrifugation and then dried at room temperature under vacuum. The conversion was determined gravimetrically. For the determination of the rate of polymerization and of the extent of cyclization, a condition of 10ml benzene solution of 0.5mol/l monomer and 0.005mol/l AIBN was used.

Extent of Cyclization

The extent of cyclization was calculated from the content of residual double bonds in polymer extraporated to 0% conversion in order to exclude the effect of the monomer concentration change from progress of the polymerization. The residual double bond was calculated from the absorbance ratio, $D_{C=C}/D_{C=O}$, of the IR spectrum(nujol mull), assuming that the absorption coefficients of $D_{C=C}$ and $D_{C=O}$ in monomer and polymer are identical. The extraporation to 0% conversion was shown in Figure 1. Because of this assumption and of the neglect of consumption of double bond other than cyclization such as branching, the extent of

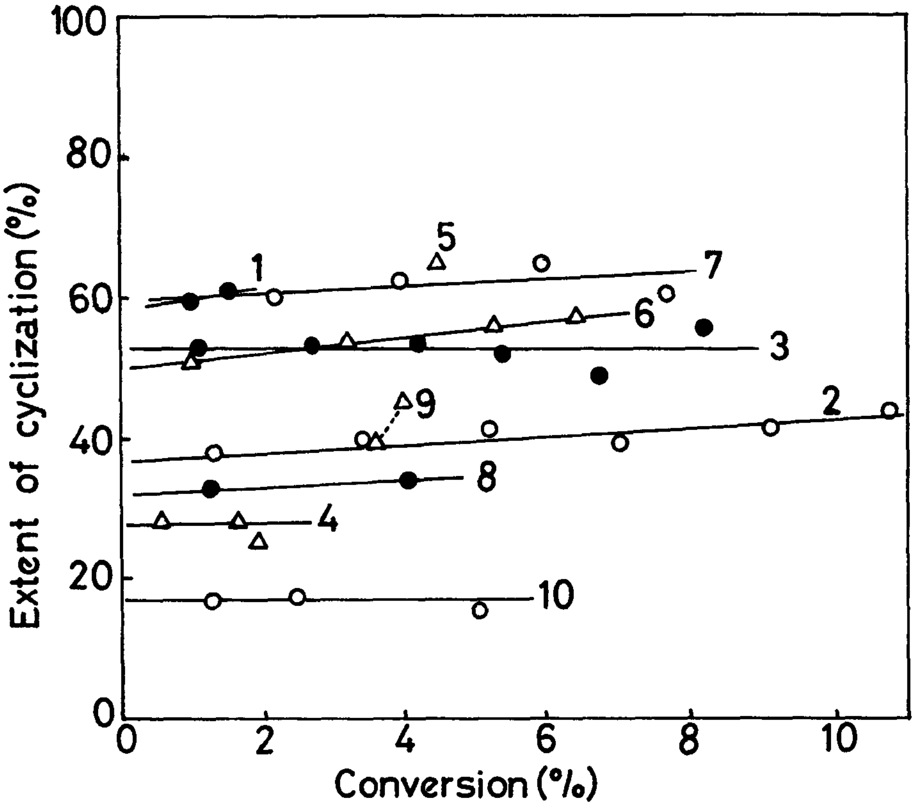


Figure 1. Extraporation of Extents of Cyclization to 0% Conversion in Radical Polymerization of Divinyl Esters

Polymerization conditions; [M]=0.50mol/l, [AIBN]=0.0050ml/l in benzene solution at 60°C $(CH_2=CHOCO)_2(CH_2)_{n-2}$, where n=1 represents divinyl carbonate.

cyclization calculated here might include a considerable error. Thus, these data might be a reasonable measure of the extent of cyclization as far as homologous monomers are concerned.

Saponification of Polymer

20ml of a 10% aqueous potassium hydroxide solution was added to 1g of swelled polymer in 20ml of acetone. Saponification was completed for a day at room temperature. After separation of inorganic ion and low molecular weight compounds by dialysis, an aqueous polymer solution was poured into a large amount of methanol, yielding a precipitate of PVA. The PVA was dried by freeze-drying of an aqueous solution.

Characterization of PVA

1,2-Glycol content was determined by titrating the periodic acid consumption by PVA in accordance with the method of Harris et al.8)

Degree of polymerization of PVA was calculated from a specific viscosity of a 1% aqueous PVA solution according to the equation presented by Nakajima9).

IR spectrum of PVA was measured with a film which was prepared from a 1% aqueous solution and dried at 30 °C in a silicagel desiccator.

Results and Discussion

Rate of Polymerization

The time-conversion curves of the polymerization of divinyl esters at 0.50mol/l benzene solution are shown in Figure 2 and the rate of polymerization are given in Table III. Figure 3 shows the rate of polymerization of each monomer, representing a periodical relationship with the methylene numbers of the monomers. Since there was no correlation to the extent of cyclization, this periodical properties in the rate of polymerization sould be ascribed to the reactivity of the vinyl group in each monomer. If the main factor of this property is the inductive effect of substituents, $CH_2=CHOCO(CH_2)_{n-2}COO-$, such variation in the rate of polymerization is not expected for the change from divinyl succinate to divinyl sebacate($n = 4 \sim 10$). Actually the spectroscopic data for the monomers, $n = 4 \sim 10$, showed a similar property of the vinyl group to one another and to vinyl acetate (Table II). The reason for this periodical property of the rate of polymerization is not yet explainable.

The plot of the extent of cyclization against the rate of polymerization is depicted in Figure 4. There seems to be two groups of monomers, one is comparatively likely to cyclize and the other is not. In each group, the increase of the polymerizability is accompanied by the decrease in the extent of cyclization.

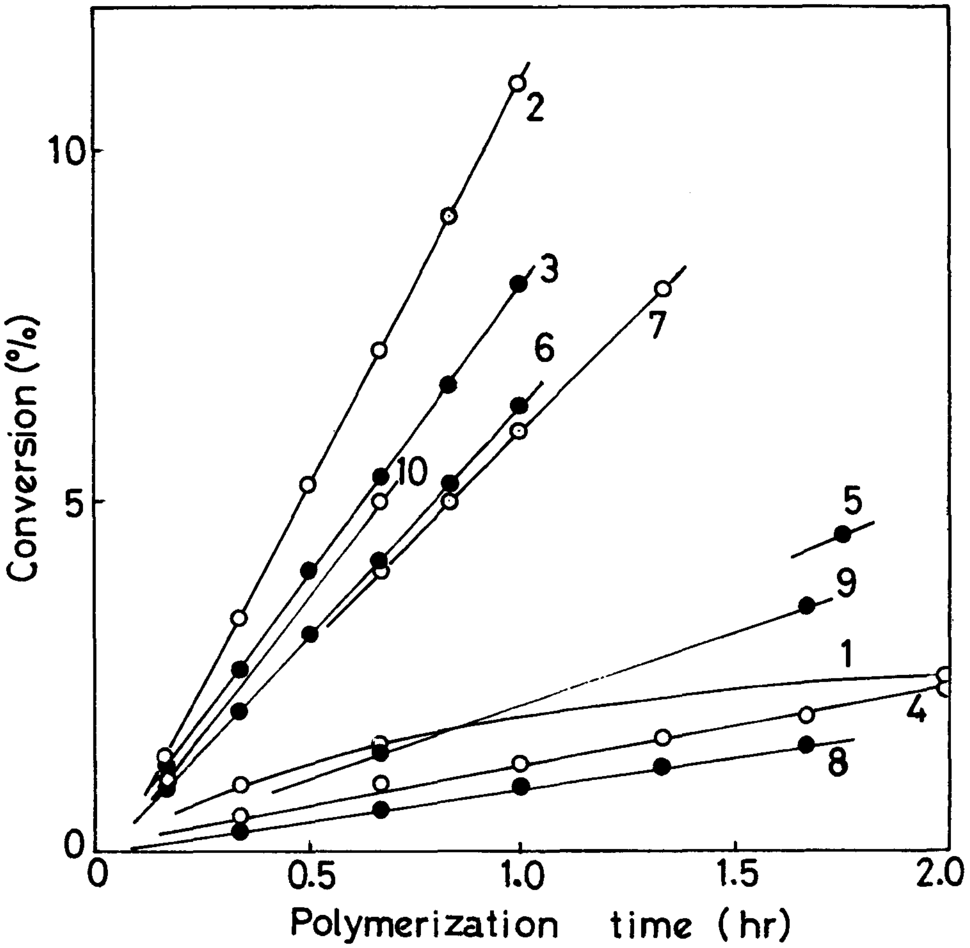


Figure 2. Time-Conversion Curves at Polymerization of Divnyl Esters

Polymerization condition is identical to those described in Figure 1.

$(CH_2{=}CHOCO)_2(CH_2)_{n-2}$, where n=1 represents divinyl carbonate.

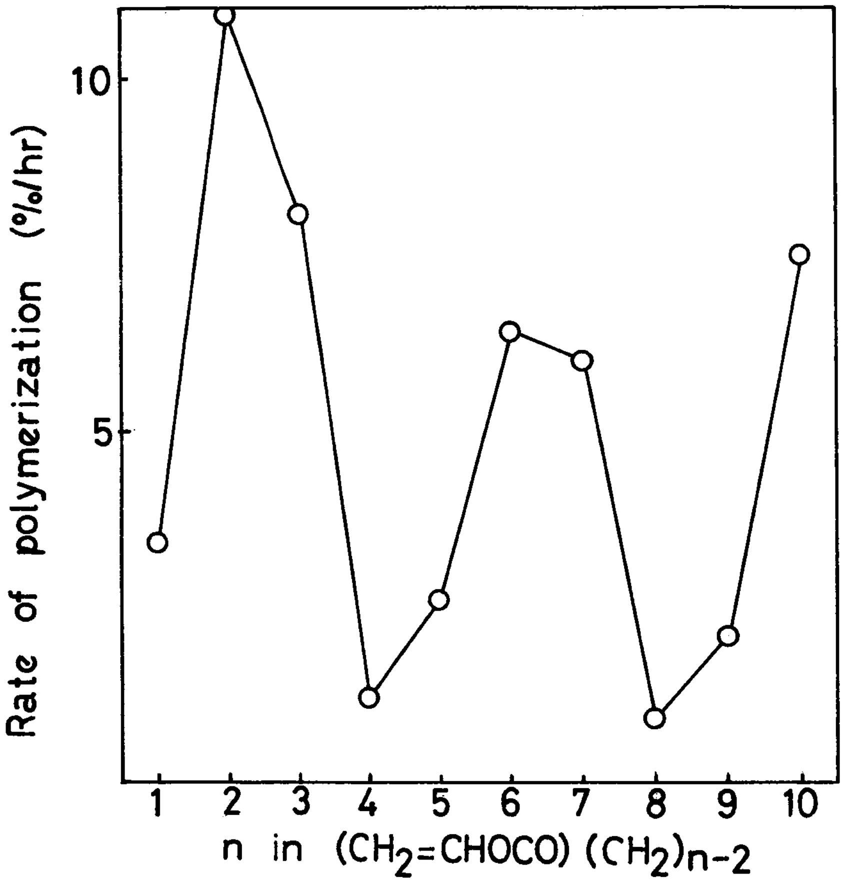


Figure 3. Rate of Polymerization of Divinyl Esters $(CH_2=CHOCO)_2(CH_2)_{n-2}$, where n=1 represents divinyl carbonate.

Table III. Rate of Polymerization and Extent of Cyclization

Polymerization condition; [M]=0.50mol/l, [AIBN]=0.0050mol/l in benzene solution at 60°C

Monomer	R_p(%/hr)	Extent of Cyclization
D.V. Carbonate	3.4	59
D.V. Oxalate	10.9	37
D.V. Malonate	8.1	63
D.V. Succinate	1.3	28
D.V. Glutarate	2.6	65
D.V. Adipate	6.4	50
D.V. Pimelate	6.0	60
D.V. Suberate	0.9	32
D.V. Azerate	2.1	42
D.V. Sebacate	7.5	17

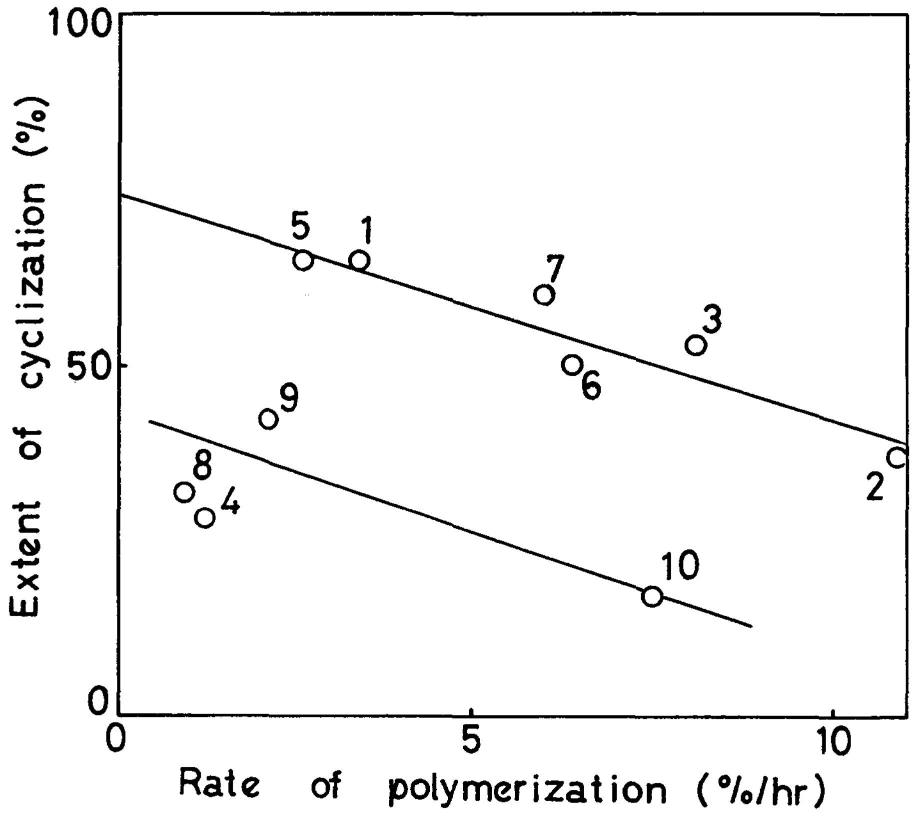


Figure 4. Correlation between Rate of Polymerization and Extent of Cyclization

Extent of Cyclization

The structure of the cyclic units in polymers is considered to be almost the head-to-tail type judging from the content of the 1,2-glycol structure in PVA described afterward. The extents of cyclization are given in Table III. Figure 5 shows an alternation of the extents of cyclization as in the melting point of dibasic acids. Although the accuracy of the absolute value of these data was not so good as described before, it is a very interesting correlation. The conformation of the monomers in solution and the stability of cyclic unit should be considered in rationalization of the alternation tendency. Dipole moment, which is considered as a measure of the conformation in solution, of diethyl esters of dibasic acids are similar to each other except for carbonate, oxalate and succinate[10]. The stability of the ring structure has not yet been known. A similar tendency of the ease of cyclization of diallyl esters of dibasic acids was expected because the structure of ring in poly(diallyl esters) resembles that in poly(divinyl esters). However, the result of bulk polymerization of diallyl esters, which was reported by Simpson and Holt and is shown in Figure 5[11], did not resemble that of divinyl esters.

Marvel et al. reported the cyclopolymerization of α-diolefins, $CH_2=CH(CH_2)_nCH=CH_2$, $n = 2 \sim 15$, with the Ziegler catalyst, $Al(i\text{-}Bu)_3$-$TiCl_4$, and the result is shown in Figure 5[12]. In the cyclopolymerization of α-diolefins, the ease of cyclization at 5 and 6

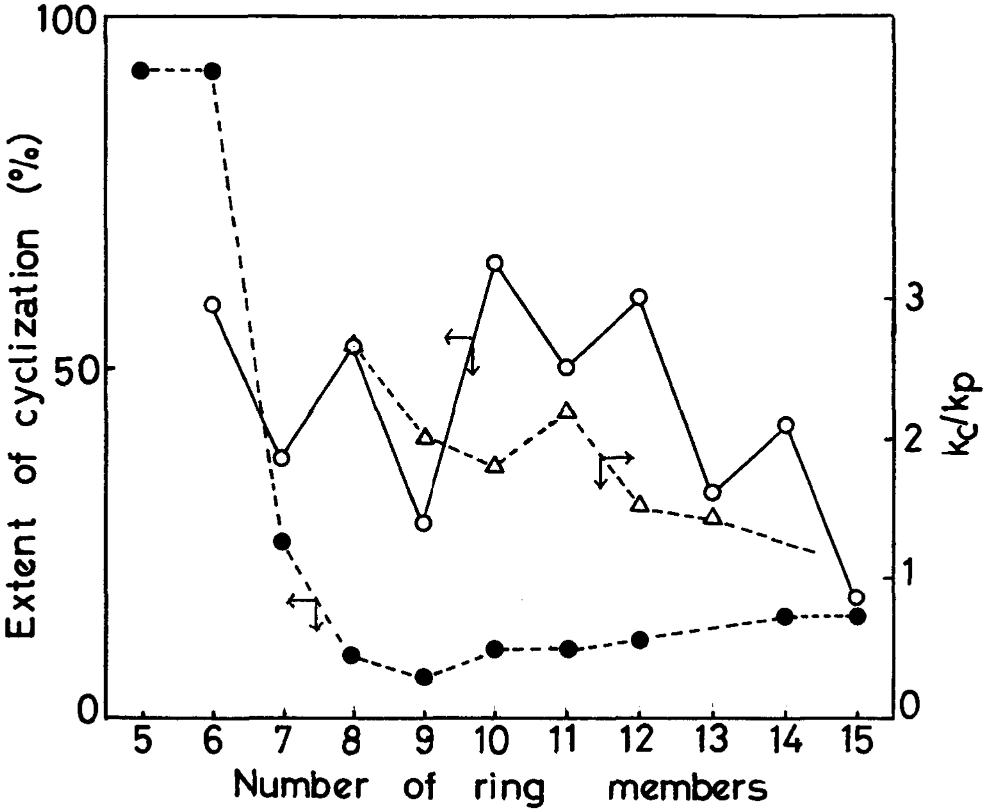


Figure 5. Extent of Cyclization in the Radical Polymerization of Divinyl Esters

○; Divinyl esters, polymerization condition is identical to those described in Figure 1.

●; -Diolefins, M 0.20mol/l, catalyst, Al(i-Bu)$_3$-TiCl$_4$ 12)

△; Diallyl esters, bulk polymerization at 80°C catalyst, benzoyl peroxide, 11) membered rings are explicable on the basis of the ring strain. On the other hand, there appeares to be not so great différence in the ring strain beween divinyl carbonate and other divinyl esters. Two methylene groups in poly(α-diolefins) are replaced by two oxygen atoms in poly(divinyl esters) and this replacement may releave steric interference, that is, it increase the ease of cyclization.

Structure and Properties of derived PVA

The properties of the PVA which was derived from the poly(divinyl esters) by saponification are given in Table IV along with the polymerization conditions. All the monomer were liable to form gelled polymers corresponding to medium cyclopolymerizability. The derived PVA showed a closely similar structure with respect to the 1,2-glycol content and stereoregularity to that from poly(vinyl acetate). As to PVA derived from poly(divinyl oxalate), it seemed likely that 1,2-glycol structure should be formed considerably if the formation of the 6-membered ring with the head-to-head linkage is preferentially expected in poly(divinyl oxalate). No difference, however, could be detected between PVA from poly(divinyl oxalate) and those from other poly(divinyl esters). Since a considerable cyclization occured as previously described, the ring closure reaction in divinyl oxalate should have yielded the 7-membered ring predominantly. This results showed that the ease of cyclization does not depend only

Table IV. PVA derived from Poly(divinyl esters)

Monomer	[M] vol%	Polymn. time hr	Conv. %	Derived PVA DP	$\frac{D_{916}}{D_{849}}$	1,2-glycol content, %
Divinyl Carbonate[a]	100	0.25	9.9	631	0.30	13.7
	10	67	-	188	0.19	42.0
	5	67	30	164	0.17	45.8
Divinyl Oxalate	20	4	80	525	0.26	3.4
	10	2	29	-	0.23	2.7
	1	50	54	132	-	3.2
Divinyl Malonate	20	16.3	91	182	0.26	4.3
	10	2	44	-	0.26	4.2
	1	50	34	-	-	-
Divinyl Succinate	20	4	72	218	0.23	3.6
	10	20	91	150	0.27	4.1
	1	50	41	-	-	-
Divinyl Glutarate	20	15	84	201	0.39	3.6
	10	20	74	138	-	3.9
	1	50	35	-	-	-
Divinyl Adipate	20	10	83	180	0.36	3.7
	10	20	80	-	0.39	3.6
	1	50	41	-	-	-
Divinyl Sebacate	20	15	83	194	0.41	3.8
	10	24	55	163	-	4.6
	1	50	17	-	-	-

a) The data is cited from reference (2), and reaction condition was similar to this paper.

on number of ring atoms. Probably divinyl oxalate has a particular conformation which is unfavorable to produce the 6-membered ring owing to the presence of neighboring two carbonyl groups.

Mizushima reported from spectroscopic measurement that two conformations occur in the case of oxalic acid derivatives, a trans and a cis form13). Ketelaar and Meurs reported the energy difference getween both conformations to be 420cal/mol for ethyl oxalate from the measure of temperature dependency of dipole moment14). Construction of the model of the 6-membered ring shows that two carbonyl groups are roughly parallel to each other taking a cis conformation, whereas the carbonyl group in 7-membered ring are roughly perpendicular to one another. Therefore, the formation of the 6-membered ring may require higher activation energy than the 7-membered ring. For this reason, the 6-membered ring hardly formed in the polymerization of divinyl oxalate.

Optical density ratio, D_{916}/D_{849}, of the IR spectrum of PVA is considered to be a measure of tacticity in case of low content of 1,2-glycol structure. The ratio showed that PVAs from poly(divinyl oxalate), malonate and succinate possess slightly higher isotactic structure than PVAs from other polymers. This result suggests that the some steric control which is probably attributed to the strained conformation of the cyclized free radical during the cyclopolymerization process of these three monomers. Whereas, the large membered ring have little ring strain and then have little steric control for the cyclopolymerization of other monomers.

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I-4

Copolymerization of Divinyl Carbonate

Synopsis

Copolymerization parameters of divinyl carbonate were determined by the copolymerization with *p*-chlorostyrene and vinyl acetate, and compared with those of ethyl vinyl carbonate. *Q* and *e* values are: Q=0.035, e=-0.23 for divinyl carbonate and Q=0.025, e=-0.26 for ethyl vinyl carbonate. These values suggest that copolymerization reactivities of divinyl carbonate and ethyl vinyl carbonate are alike each other and are close to that of vinyl acetate(Q=0.026, e=-0.22). Since divinyl carbonate undergoes a cyclization polymerization to considerable extents, the data also suggest that there is no extraordinary effect of the cyclization on copolymerization parameters. Extent of cyclization of divinyl carbonate was found to be lower in the divinyl carbonate-*p*-chlorostyrene copolymer than in the divinyl carbonate-vinyl acetate copolymer.

〔112〕 炭酸ジビニルの共重合

（1967年6月27日受理）

菊川　清*・野桜俊一*・村橋俊介*

要　旨　炭酸ジビニル（DVC）の共重合パラメーターを *p*-クロルスチレン（*p*-ClSt）および酢酸ビニル（VAc）と共重合させて決定した。また，これらの値を炭酸エチルビニル（EVC）のそれと比較した。Q，e 値は各々，DVCについて，$Q=0.035$，$e=-0.23$，EVCについて，$Q=0.025$，$e=-0.26$ である。これらの値から，DVCとEVCは互いによく似た共重合反応性を示し，VAc（$Q=0.026$，$e=-0.22$）によく似ていることがわかった。DVCはかなり環化重合を行なうので，この結果はまた，環化反応が共重合パラメーターに対し特別な影響を及ぼさないことを示していると思われる。DVC-*p*-ClSt 系の共重合体中では，DVC-VAc 系の場合よりも環化率が低いことがわかった。

1. 緒　言

2個の官能基をもつ炭酸ジビニルは環化重合を行なって，環状構造をもつポリマーを得る可能性がある。さらにその加水分解により得られるPVAは環状構造に由来する特異な化学構造および立体構造を期待することができる。このような観点から，前報[1]において，モノマーの合成法および重合性，特に環化重合に及ぼす重合条件の影響を検討した。すなわち，炭酸ジビニルはラジカル重合によりペンダント二重結合，6員環および5員環カルボナートの3種の構造単位からなるポリマーを生成することを推定した。重合温度によりこれら構造単位間の相対量は著しく変化するが，重合率，溶媒の変化によってはポリマー構造に大きな変化は見られなかった。

本報では，炭酸ジビニルの一般的重合性を知るために共重合を行なって共重合パラメーター，Q，e 値を求めた。相手モノマーとしては，ポリマーの組成分析の容易な *p*-クロルスチレン，および反応性のよく似ていると思われる酢酸ビニルを選んだ。

さらに炭酸ジビニルにおいて同一分子中に2個のビニル基があるための効果をみるために，炭酸エチルビニルの共重合反応性を調べ比較した。

2. 実　験

2.1 モノマー，溶媒

炭酸ジビニルは前報に記したようにホスゲンと水銀ジアセトアルデヒドより合成した[1]。bp 44.7～45.3°C/85 mmHg。

炭酸エチルビニルはエチルクロルカルボナートと水銀ジアセトアルデヒドより同様に合成した。bp 69.5°C/147 mmHg（108.5～108.6°C）

p-クロルスチレンは *p*-クロルアセトフェノンを Al(*i*-PrO)$_3$ により還元し，活性アルミナを用いて熱分解脱水して得た。bp 35.0～35.2°C/3 mmHg。

酢酸ビニルは市販品を NaHSO$_3$ 水溶液で洗浄し，さらに水洗して，CaCl$_2$ で乾燥後，Widmer の蒸留塔で蒸留した。bp 72.3°C。

モノマーはすべてガスクロマトグラフ（TCP カラム）により不純物のないことを確かめて用いた。

ベンゼンは常法により精製した。アセトンは KMnO$_4$ を加え，1昼夜加熱還流後，蒸留して用いた。

2.2 共　重　合

炭酸ジビニルは2官能基をもつモノマーであるので，モノマー1分子を2当量として以下の実験を行なった。

ガラスアンプルへ所定のモノマー濃度のベンゼン溶液をピペットで仕込み（炭酸エチルビニル－*p*-クロルスチレン系のみ塊重合）真空系（$<10^{-3}$ mmHg）で3回脱気した後，封管し，60±0.05°C の恒温槽で静置重合した。所定の時間重合した重合溶液を大量の沈殿剤（炭酸ジビニル-*p*-クロルスチレン系ではメタノール，他は *n*-ヘキサンまたは石油エーテル）へ注ぎ，数回の decantation をくり返したのち，炭酸ジビニルの系では有機溶媒に不溶であるので遠心分離し，沈殿剤により洗浄をくり返したのち，これを減圧乾燥して秤量，重合率を求めた。炭酸エチルビニルの系では，ポリマーをベンゼンに溶かし，凍結乾燥して重合率を求めた。重合率は炭酸エチルビニル-酢酸ビニルの系以外は10％以下にとどめた。炭酸エチルビニル-酢酸ビニルの系ではわずかに10％をこえたが，モノマー組成とポリマー組成との間にほとんど差がないので，共重合組成式の微分式をそのまま用いた。

2.3 共重合体の組成分析

p-クロルスチレンの共重合系では，ポリマー中の塩素の元素分析より，ポリマー中の *p*-クロルスチレンのモル分率を求めた。酢酸ビニルの共重合系では，ポリマーのアセトン溶液（炭酸ジビニルの多いポリマーでは不溶部があるが，加水分解に影響はない）にカセイソーダ水溶液を加えて加水分解し，生じた酢酸ソーダを過剰の塩

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酸を加えて酢酸とし，カセイソーダで，pH メーターを用いて中和滴定した。これよりポリマー中の酢酸ビニルのモル分率を求めた。

2.4 共重合体の IR スペクトル

炭酸ジビニルの共重合系より得られるポリマーはフィルム形成能がないので，KBr 錠剤法により測定した。炭酸エチルビニルの系ではフィルムにより測定した。

3. 結　　果

共重合結果を Table 1〜4 に示した。

3.1 モノマー反応性比 r_1，r_2

r_1，r_2 の決定には Fineman-Ross 法，および交点法を用いたが，p-クロルスチレン-炭酸ジビニルの系では，Fineman-Ross 法より求めた r_1，r_2 より得られる共重合組成曲線が実測値とかなりずれたので，曲線合致法により求めた。それらの値をまとめて Table 5 に示した。

Table 1. Copolymerization of *p*-chlorostyrene (M_1) and divinyl carbonate (M_2).
$[M_1]+[M_2]=2$ mol/l in benzene,
[AIBN]$=0.01$ mol/l, 60°C

Expt. No.	M_2 mole fraction in monomer	Polymerization time (hr)	Conversion (%)	M_2 mole fraction in polymer
1	0.952	45.0	2.73	0.436
2	0.900	22.5	6.00	0.234
3	0.700	7.0	7.92	0.083
4	0.600	5.0	7.40	0.053
5	0.400	3.0	6.47	0.020
6	0.200	2.0	5.47	0.017

Table 2. Copolymerization of vinyl acetate (M_1) and divinyl carbonate (M_2).
$[M_1]+[M_2]=2$ mol/l in benzene,
[AIBN]$=0.01$ mol/l, 60°C

Expt. No.	M_2 mole fraction in monomer	Polymerization time (hr)	Conversion (%)	M_2 mole fraction in polymer
7	0.100	2.5	9.16	0.126
8	0.300	2.5	8.07	0.359
9	0.500	2.5	6.67	0.567
10	0.600	2.5	6.99	0.668
11	0.700	2.5	6.76	0.746
12	0.900	2.5	5.97	0.839
13	0.506	2.0	4.13	0.572

Table 3. Bulk copolymerization of *p*-chlorostyrene (M_1) and ethyl vinyl carbonate (M_2).
[AIBN]$=0.5$ mol %/monomer, 60°C

Expt. No.	M_2 mole fraction in monomer	Polymerization time (hr)	Conversion (%)	M_2 mole fraction in polymer
14	0.911	1.5	2.38	0.216
15	0.784	1.25	3.11	0.0762
16	0.685	1.0	1.71	0.0483
17	0.609	1.25	5.67	0.0401
18	0.401	1.25	8.66	0.0322
19	0.921	5.0	2.85	0.219
20	0.961	5.0	1.03	0.376
21	0.977	24.0	4.15	0.600

Table 4. Copolymerization of vinyl acetate (M_1) and ethyl vinyl carbonate (M_2).
$[M_1]+[M_2]=2$ mol/l in benzene,
[AIBN]$=0.01$ mol/l, 60°C

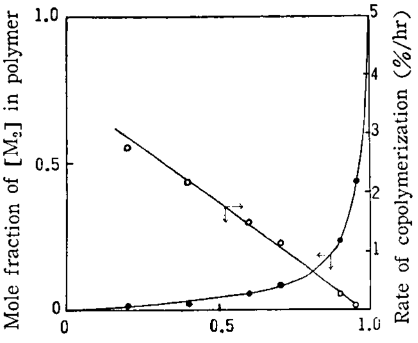
Expt. No.	M_2 mole fraction in monomer	Polymerization time (hr)	Conversion (%)	M_2 mole fraction in polymer
22	0.901	3.10	7.45	0.894
23	0.701	3.17	0.81	—
24	0.601	3.17	9.66	0.586
25	0.501	3.10	9.76	0.487
26	0.401	3.17	10.53	0.395
27	0.301	3.17	11.13	0.309
28	0.201	2.00	7.25	0.213
29	0.101	3.10	11.89	0.117

Table 5. Monomer reactivity ratios.

M_1	M_2	r_1	r_2
p-ClSt	DVC	27.5	0.036
VAc	DVC	0.77±0.05	1.33±0.08
p-ClSt	EVC	39.8±0.7	0.025±0.017
VAc	EVC	0.87±0.04	0.79±0.07

また Table 5 の r_1，r_2 の値より得られる共重合組成曲線と実測値のプロットを Fig. 1〜4 に示した。Fig. 1〜4 には同時に，共重合速度をモノマー組成についてプロットしたものも示した。

3.2 Q，e 値

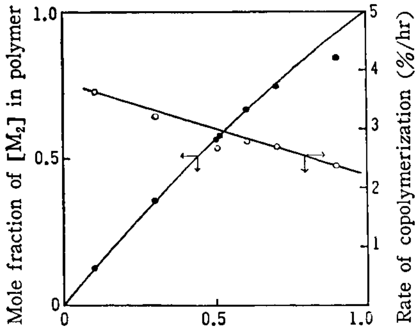


Mole fraction of [M_2] in monomer

●: The curve was calculated for $r_1=27.5$, $r_2=0.036$.

○: Rate of copolymerization $[M_1]+[M_2]=2\ mol/l$, $[AIBN]=0.01\ mol/l$ in benzene at 60°C

Fig. 1. Copolymer composition curve and rate of copolymerization for the system: divinyl carbonate (M_2)-*p*-chlorostyrene (M_1).



Mole fraction of [M_2] in monomer

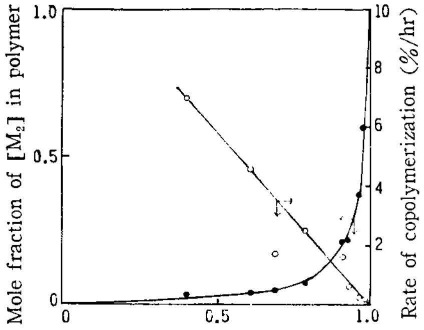
●: The curve was calculated for $r_1=0.77$, $r_2=1.33$.

○: Rate of copolymerization $[M_1]+[M_2]=2\ mol/l$, $[AIBN]=0.01\ mol/l$ in benzene at 60°C

Fig. 2. Copolymer composition curve and rate of copolymerization for the system: divinyl carbonate (M_2)-vinyl acetate (M_1).

Table 6. *Q-e*, values.

M_1	M_2	Q_2	e_2
p-ClSt	DVC	0.036	−0.23
VAc	DVC	0.034	−0.22
p-ClSt	EVC	0.025	−0.26
VAc	EVC	0.026	+0.39

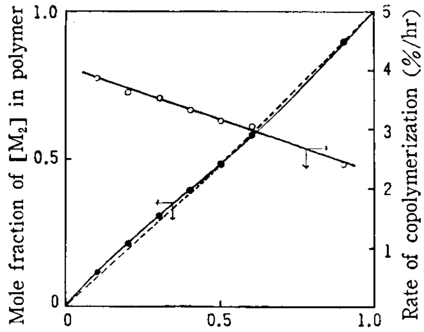


Mole fraction of [M_2] in monomer

●: The curve was calculated for $r_1=39.8$, $r_2=0.025$.

○: Rate of copolymerization Bulk copolymerization, $[AIBN]=0.5$ mol%/monomer at 60°C

Fig. 3. Copolymer composition curve and rate of copolymerization for the system: ethyl vinyl carbonate (M_2)-*p*-chlorostyrene (M_1).



Mole fration of [M_2] in monomer

●: Solid line was calculated for $r_1=0.87$, $r_2=0.79$.

Dashed line was calculated for $r_1=1.03$, $r_2=0.97$.

○: Rate of copolymerization $[M_1]+[M_2]=2\ mol/l$, $[AIBN]=0.01\ mol/l$ in benzene at 60°C

Fig. 4. Copolymer composition curve and rate of copolymerization for the system: ethyl vinyl carbonate (M_2)-vinyl acetate (M_1).

Q, *e* の値を Table 5 の r_1, r_2 値より求めた。*p*-クロルスチレンの $Q=1.03$, $e=-0.33$, および酢酸ビニルの $Q=0.026$, $e=-0.22$ の値を用いた2)。その結果を Table 6 に示した。炭酸エチルビニル-酢酸ビニルの系から得られた炭酸エチルビニルの *e* の値が他のそれと大きく違うが，これは r_1 および r_2 の微少な違いが *e* に大

きく効いているためであろう。たとえば，炭酸エチルビニルのQ，e値を炭酸エチルビニル-p-クロルスチレンの系から得られた $Q=0.025$，$e=-0.26$ とすると，酢酸ビニルとの系では $r_1=1.03$，$r_2=0.97$ となり，この値から求めた共重合組成曲線もまた実測値と大きくはずれない（Fig. 4 の点線）。

3.3 共重合体の IR スペクトル

Fig. 5~7 に見られるようにすべての共重合体の IR スペクトルは，各単独重合体の IR スペクトルを重ね合わせたスペクトルを示した。すなわち共重合体の構造として，単独重合におけるように¹⁾，（1）式，（2）式に示した各構造単位の存在が予想される。

Table 7. Structure of DVC-*p*-ClSt copolymers.

Expt. No.	*p*-ClSt (mol %)	Pendant vinyl carbonate (mol %)	6-membered ring carbonate (mol %)	5-membered ring carbonate (mol %)
1	72	15	8.0	5.1
2	87	6.8	4.9	1.5

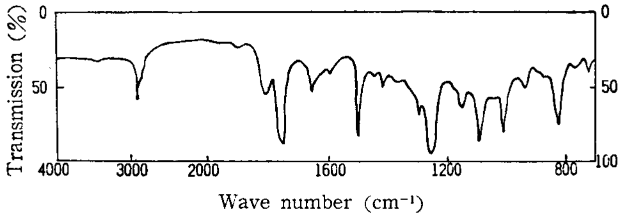


Fig. 5. IR spectrum of copolymer of divinyl carbonate with *p*-chlorostyrene, expt. No. 1.

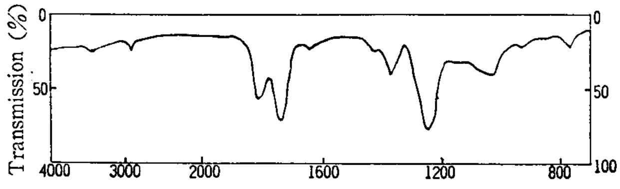


Fig. 6. IR spectrum of copolymer of divinyl carbonate with vinyl acetate, expt. No. 11.

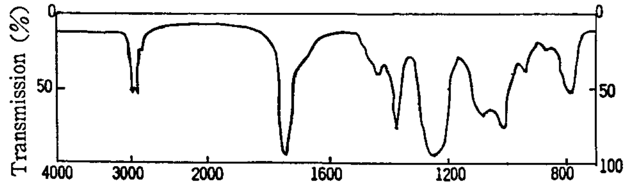
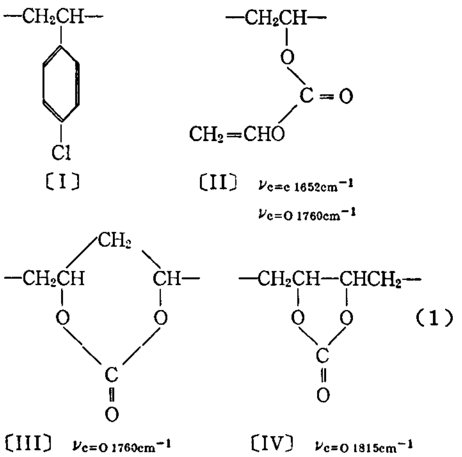


Fig. 7. IR spectrum of copolymer of ethyl vinyl carbonte with vinyl acetate, exp. Not 27.

炭酸ジビニル-p-クロルスチレン



炭酸エチルビニル - 酢酸ビニル

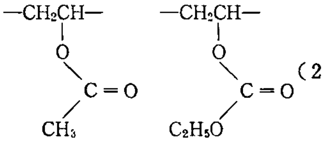


Fig. 5 に見られるように，（I）式において，〔II〕，〔III〕および〔IV〕の各構造単位の特徴的な吸収，1815 cm^{-1}，1760 cm^{-1} および 1652 cm^{-1} のある領域に〔I〕に基く吸収がないので，前報で報告した方法により¹⁾〔II〕~〔IV〕の各構造単位のポリマー中のモル%を推定できる。その結果を Table 7 に示した。

炭酸ジビニル-酢酸ビニルの系（Fig. 6）では，酢酸ビニルのカルボニルの吸収が 1740 cm^{-1} にあるため，炭酸ジビニルの構造解析は行なえない。しかし，同一温度では 5 員環カルボナートと 6 員環カルボナートの生成比はだいたい一定と考えられるので（たとえば前報¹⁾ の結果を参照）ポリマー中の環化率は定性的に，ペンダント二重結合の吸収 1652 cm^{-1} の吸光度と 5 員環カルボナートの吸収，1815 cm^{-1} の吸光度を比較して知ることができる。この吸光度比を炭酸ジビニル-p-クロルスチレン，炭酸ジビニル - 酢酸ビニルおよび炭酸ジビニル単独重合体について比較したのが Table 8 である。相手モノマーにより環化率に変化

Table 8. Structural variations of divinyl carbonate units in copolymers.
Monomer concentration 2 mol/*l* in benzene, 60°C

Expt. No.	DVC-VAc copolymer			DVC-*p*-ClSt copolymer		DVC homopolymer
	7	10	12	1	2	
$\frac{D_{1815}}{D_{1652}}$	10	10	3.8	1.4	0.45	5.4

のあることがわかる。

4. 考　察

環化重合をするモノマーの共重合については，その重合様式が多様であるため，共重合反応は複雑となり，正確な共重合組成式を求めることはかなり困難である。環化の様式を一つしかもたないモノマー（たとえば無水アクリル酸のように6員環が唯一の環構造と考えられるモノマー）では，Smets ら[3] および Gibbs ら[4] によってその共重合組成式が求められている。

炭酸ジビニルでは，ポリマーの IR スペクトルから，ポリマー中にペンダントビニルカルボナート，6員環および5員環カルボナートの3種の構造単位が認められている。ここで，共重合体成長反応の素反応のうち，橋かけ反応を無視し，また，5員環，および6員環カルボナートの生成比を一定として，その合計を環構造としてまとめると，結局，Smets らの取扱いと同等となる[3]。ここで前者の仮定は，重合率を低くおさえているので妥当であろう。また後者の仮定も，同一温度では5員環と6員環の生成比が重合条件によらずほぼ一定である[1] ので妥当である。すなわち，動力学的連鎖長が十分に大であることおよび，各ラジカルの定常状態が成立すれば，共重合組成式として（3）式を導くことができる[3]。

$$\frac{d[\mathrm{M}_1]}{d[\mathrm{M}_2]} = \frac{[\mathrm{M}_1]}{[\mathrm{M}_2]} \times \left\{ \frac{r_1[\mathrm{M}_1]+[\mathrm{M}_2]+K_c\left(\dfrac{r_1[\mathrm{M}_1]+[\mathrm{M}_2]}{r_c[\mathrm{M}_2]+[\mathrm{M}_1]}\right)}{r_2[\mathrm{M}_2]+[\mathrm{M}_1]+K_c} \right\} \quad (3)$$

ここで $r_c=k_{c2}/k_{c1}$（環ラジカルに対するモノマー M_1, M_2の反応性化）$K_c=k_c/k_{21}$（M_2 ラジカルに M_1 モノマーが付加する速度に対する，M_2 ラジカルの環化する速度）である。

（3）式は次の三つの条件のいずれか成立すれば，Mayo-Lewis の共重合組成式と同等である。

1） $K_c \fallingdotseq \infty$ $(1/K_c \fallingdotseq 0)$ すなわち，ほとんど環化する場合

2） $K_c \fallingdotseq 0$，ほとんど環化しない場合

3） $r_c=r_2$，環ラジカルに対するモノマー M_1, M_2の反応性比が，M_2 ラジカルに対するそれと変わらないとき，

炭酸ジビニルでは，1）も2）も成立しない，また，共重合体中では正確な環化率を求めることは困難である。そこで2）の条件の成立を仮定して，Mayo-Lewis の共重合組成式を用いて，モノマー反応性 r_1, r_2 を求めた。Table 6 に見られるように，このようにして求めた r_1, r_2 より得られる Q および e 値が相手モノマーが変わって，その環化率が変化しても，よい一致を示すことから，上の仮定の妥当性を示していると思われる。

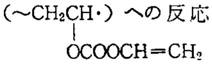
Table 5, 6, Fig. 2, 4 に見られるように，炭酸ジビニル，炭酸エチルビニルとも酢酸ビニルに非常によく似た重合反応性を示すことがわかった。これは -OCOOR と -OCOR との間には，ビニル基に与える効果についてはほとんど差のないことを示している。

炭酸ジビニルと炭酸エチルビニルとの間の Q の値のわずかな違いは，その原因として次の二つが考えられる。

i） 環化反応による効果

ii） 置換基効果

i）の環化反応による効果は，Table 8 に見られるように，その環化率が相手モノマーによりかなり影響されていると思われるにもかかわらず，相手モノマーの変化により Q の値に差のないことから考えにくい。ii）の置換基効果についても，置換基の違いがビニル基よりかなり離れているために大きくはないであろうが，ビニル基とエチル基の間の違いが出て来ていると思われる。すなわち炭酸ジビニルと炭酸エチルビニルの間に大きな差がないことから，同一分子中に2個のビニル基があるための特別な効果はないことが推定される。

Table 8 に見られるように，炭酸ジビニルの環化反応におよぼす相手モノマーの影響はかなり著しいと思われる。すなわち，ペンダントビニルカルボナートを基準とした5員環カルボナートの生成割合は，前述のように定性的に環化率を示すと考えられるが，この値は，炭酸ジビニル-酢酸ビニル≧炭酸ジビニル単独＞炭酸ジビニル-*p*-クロルスチレンの順であることがわかった。これは各モノマーの M_2 ラジカル末端  $(\sim\mathrm{CH_2}\underset{\substack{|\\ \mathrm{OCOOCH{=}CH_2}}}{\mathrm{CH}}\cdot)$ への反応性から推定できる。すなわち Table 5 の r_2 の値 から，M_2 ラジカル末端への各モノマーの反応性は，炭酸ジビニルを基準として，*p*-クロルスチレン≈28，炭酸ジビニル=1，酢酸ビニル≈0.75 である。M_2 ラジカル末端が環化する確率は，酢酸ビニルとの共重合で最も大きく，*p*-クロルスチレンとの共重合で小さいと考えられることと矛盾しない。

付 記： 本研究の一部は第12回高分子研究発表会

(神戸, 1966年) において発表した。

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Copolymerization of Divinyl Carbonate

By Kiyoshi Kikukawa*, Shun'ichi Nozakura* and Shunsuke Murahashi*

Copolymerization parameters of divinyl carbonate (DVC) were determined by the copolymerization with *p*-chlorostyrene (*p*-ClSt) and vinyl acetate (VAc), and compared with those of ethyl vinyl carbonate (EVC). Q and e values are: $Q=0.035$, $e=-0.23$ for DVC and $Q=0.025$, $e=-0.26$ for EVC. These values suggest that copolymerization reactivities of DVC and EVC are alike each other and are close to that of VAc ($Q=0.026$, $e=-0.22$). Since divinyl carbonate undergoes a cyclization polymerization to considerable extents, the data also suggest that there is no extraordinary effect of the cyclization reaction on copolymerization parameters. Extent of cyclization of DVC was found to be lower in the DVC-*p*-ClSt copolymer than in the DVC-VAc copolymer.

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Chapter II

Effect of 1,2-Glycol Structure and Stereoregularity of Poly(vinyl alcohol) on Poly(vinyl alcohol)-Iodine Reaction

Synopsis

The poly(vinyl alcohol)-iodine blue color reaction in dilute aqueous solution has been investigated at 6-8 °C and extinctions at the absorption maximum have been measured as a function of the 1,2-glycol content and stereoregularity of poly(vinyl alcohol) (PVA). The increase of the 1,2-glycol content and of isotacticity remarkably decreased the color intensity. Particularly, when the 1,2-glycol content was larger than 5mol% or isotacticity was more than 70%, the reaction mixture was almost colorless. Wave length of the absorption maximum of the reaction mixture was not affected by the 1,2-glycol content(608mμ), whereas the maximum was shifted to shorter wave length by the increase of isotacticity. It is suggested that the 1,2-glycol structure simply decreased the content of the PVA-iodine complex. Sequence length of 1,3-glycol units required for the color reaction of atactic PVA was estimated to be about 120. Isotactic structure,

on the other hand, may not only disturb the formation of the complexes, but may also affect its structure.

Introduction

Various physical properties of poly(vinyl alcohol)(PVA) may be affected by molecular weight, 1,2-glycol structure, residual acetate group, branching, stereoregularity etc. PVA samples with different stereoregularities have been prepared in order to study qualitatively the effect of stereoregularity on crystallinity, solubility to water and so on$^{1)}$. It has also been informed that the increase of the 1,2-glycol content lowers the melting point of PVA and deteriorates crystallinity$^{2)}$.

The blue color reaction of PVA with iodine proceeds in a similar manner to the amylose-iodine reaction. The intensity of the blue color was known to vary delicately with various kinds of PVA specimens and the fact has been interpreted to be due to minor changes in the molecular structure of PVA. Among many structural variations, the effect of molecular weight has been studied quantitatively$^{3)}$.

The present study was undertaken to elucidate the role of the 1,2-glycol structure and stereoregularity on the PVA-iodine reaction. During the course of our study Shibatani et al. reported the effect of these variables on the color intensity of the PVA-iodine reaction[4]. We have obtained further informations about the position of the absorption maximum in addition to the intensity. The nature of the complex will be discussed on this basis.

Experimental

Preparation of Polymers

PVA samples with different 1,2-glycol contents were prepared by hydrolyzing copolymers of vinyl acetate and divinyl carbonate. Polymerization was carried out in methanol at 1 °C using a monomer concentration of 2mol/l and triisobutylboron as a catalyst. The results of copolymerization are given in Table I and Figure 1, and the degree of polymerization and the 1,2-glycol content of resulting PVA are given in Table II. Monomer reactivity ratios are found to be $r_{VAc}=0.41$ and $r_{DVC}=1.55$. Former values in the presence of azobisisobutyronitrile as catalyst are 0.77 and 1.33, respectively[5].

PVA samples with 1,2,3-triol structure were prepared by hydrolyzing a copolymer of vinyl acetate and vinylene carbonate. Polymerization conditions are the same as in the vinyl acetate-divinyl carbonate copolymerization. The degree of polymerization and the 1,2,3-triol content of resulting PVA are given in Table III.

PVA samples with different stereoregularity were prepared using various polymerization conditions and starting monomers. Polymerization conditions are summarized in Table IV. Stereoregularity and degree of polymerization are given in Tables V and VI.

Determination of 1,2-Glycol Content in PVA

1,2-Glycol content was determined by titrating the periodic acid consumption by PVA in accordance with the method of Harris et al.6) It was assumed that the -CH(OH)-CH(OH)-CH(OH)- structure, formed by the copolymerization of vinylene carbonate and vinyl acetate, may consume 2 moles of periodic acid, and thus the triol structure was regarded as one 1,2-glycol structure.

Dtermination of Tacticity

Triad tacticity was determined from NMR spectra of poly-(vinyl acetate) derived from PVA samples using a JNM 4-100 spectrometer of Japan Electron Optics Laboratory Co. Ltd.7) In some cases diad tacticity was calculated from the absorbance ratio, D_{916}/D_{849}, of IR spectra of PVA films according to the equation presented by Murahashi et al7).

The PVA-Iodine Color Reaction

An aqueous PVA solution was mixed with a KI-I_2 solution at 6-8°C and kept at this temperature for 20hrs and the mixture was subjected to spectroscopic measurement at room temperature using a Hitachi spectrophotometer, EPS-3T.

Results

Influence of the 1,2-Glycol Structure on the PVA-Iodine Reaction

Table II and Figure 2 show the influence of 1,2-glycol content on the PVA-iodine reaction. The 1,2-glycol structure extensively reduced the intensity of the blue color of the reaction mixture. Particularly, it is to be noted that the position of the absorption maximum was unaltered(608mμ) and that PVA in which 1,2-glycol content is more than 5mol% was unable to develop the color. The absorption maximum shifted to 680mμ when boric acid was added.

Influence of Stereoregularity

Tables V and VI show the coloring abilities of PVA samples with various stereoregularities. The difference in stereoregularity markedly affected the PVA-iodine reaction, and particularly the PVA samples with diad syndiotacticity less than 30% did not have any visible absorption at all. The coloring ability in this case mainly depends on the increase of syndiotacticity.

It is characteristic that the PVA samples with approximately 40% syndiotacticity had the absorption maximum at a shorter wave length than the PVA samples with higher syndiotacticity. The syndiotacticity higher than 44% almost unaltered the absorption maximum and the increase in syndiotacticity resulted in the increase in extinction.

Table I. Copolymerization of vinyl acetate(M_1) and divinyl carbonate(M_2).

$[M_1]+[M_2]=2$mol/l in methanol, Catalyst; triisobutylboron 0.5mmol, at 1°C.

Exp. No.	M_2 mole fraction in monomer a)	Polymerization time, hr	Conversion %	M_2 mole fraction in copolymer a)
3	0.194	3	15.1	0.337
4	0.291	2.7	6.4	0.506
5	0.390	2.7	11.9	0.551
6	0.490	2.5	16.0	0.630
7	0.590	2.3	19.7	0.720
8	0.691	2.2	18.6	0.786
9	0.793	2	19.0	0.866
10	0.896	2	18.7	0.908

a) One mole of divinyl carbonate was regarded as two equivalent

Table II. The effect of the 1,2-glycol structure on the PVA-iodine reaction

Sample No.	1,2-glycol mol%	DP	$\frac{D_{916}}{D_{849}}$	Extinction(D_{608})a) I	II	III
1	1.41	623	0.35	3	1.88	-
2	1.87	631	0.40	2.8	1.41	-
3	2.73	518	0.34	1.08	0.50	-
4	3.17	-	-	-	-	-
5	4.09	342	0.29	0.26	-	0.83
6	4.69	335	0.29	0.11	-	0.47
7	5.09	310	0.26	0.048	-	0.19
8	5.67	332	0.29	0.026	-	0.14
9	5.17	-	0.27	0.013	-	0.037
10	6.66	290	-	0.009	-	0.017
Commercial	2.10	500	0.36	2.48	1.10	-

a) Reaction condition:

I: [PVA]=25mmol/l, [I_2]=1.25mmol/l, [KI]=2.5mmol/l, 20hrs, 6-8°C

II: [PVA]= 14.5mmol/l, [I_2]=0.87mmol/l, [KI]=1.75mmol/l, 24hrs, 6-8°C

III: Two ml of an 0.5mol/l aqueous boric acid solution was added to 7ml of the reaction mixture of I and allowed to react for 24hrs at 6-8°C

Table III. The effect of the 1,2,3-triol structure on the PVA-iodine reaction

Sample No.	1,2,3-triol mol%	DP	$\frac{D_{916}}{D_{849}}$	Extinction [a)] (D_{607})
11	2.13	617	0.37	1.60
12	10.9	392	0.28	0.22
13	11.6	604	0.29	0.09
14	18.7	408	0.23	0.03

a) Reaction condition:

[PVA]=30mmol/l, [I_2]=1.25mmol/l, [KI]=5mmol/l, 20hrs, 6-8 °C

Table IV. Preparation of PVA samples with different stereoregularities

Sample No.	Monomer[a)]	Catalyst	Solvent	Polymerization temperature, °C	Yield %
21	VOSi[b)]	$EtAlCl_2$[c)]	Toluene	-95	-
22	"	"	Toluene-CH_2Cl_2 (8:2)	-78	86
23	"	"	" (6:4)	"	58
24	"	"	" (4:6)	"	53
25	"	"	" (5:5)	"	100
26	"	"	" (3:7)	"	59
27	"	"	CH_2Cl_2	"	100
28	"	"	"	-95	-
29	"	"	"	-78	-
30	"	"	"	-60	-
41	VAc	AIBN-UV[d)]	Methanol	30-31	81.5
42	"	"	Hexane	"	87.7
43	"	"	Methanol	6-8	25.8

a) Monomer concentration was 20 vol%.

b) Vinyl trimethylsilyl ether.

c) Catalyst concentration was 0.0125mol/l.

d) Photosensitized polymerization.

Table V. The effect of stereoregularity on the PVA-iodine reaction

Sample No.	DP	Syndiotacticity diad, % [c]	Extinction[a] I λ max	Extinction[a] I D_{max}	Extinction[a] II λ max	Extinction[a] II D_{max}
21	2322	12	none	-	400-600 broad peak	0.33-0.34
22	1520	20	none	-	"	0.1-0.2
23	1485	29	none	-	-	-
24	678	39	562	0.27	-	-
25	1171	40	571	0.27	650	0.61
26	1010	44	620	0.31	-	-
27	858	55	(616)[b]	(1.06)[b]	654	2.21

a) Reaction conditions:

I: [PVA]=14.0mmol/l, $[I_2]$=2.00mmol/l, [KI]=3.00mmol/l, 6-8 °C, 20hrs.

II: [PVA]=7.0mmol/l, $[I_2]$=0.33mmol/l, [KI]=0.5mmol/l, $[H_3BO_3]$=100mmol/l 6-8 °C, 20hrs.

b) $[I_2]$=0.667mmol/l, [KI]=1.00mmol/l, other conditions are the same as I.

c) Diad tacticity was calculated from the absorbance ratio, D_{916}/D_{849}, of IR spectra of PVA films[7].

Table VI. The effect of stereoregularity on the PVA-iodine reaction

Sample No.	DP	Stereoregularity,%					Extinction b)	
		diad a)		triad				
		i	s	I	H	S	λ max	D_{max}
28	2680	55	45	36	39	25	616	0.57
29	180	49	51	26	46	28	620	1.07
30	490	48	52	25	47	28	624	1.03
41	1995	53	47	28	49	23	617	0.71
42	2080	55	45	31	48	21	618	0.69
43	3127	53	47	29	48	23	620	0.81

a)Diad tacticity was calculated from the triad tacticity.

b) Reaction condition:

[PVA]= 6.25mmol/l, [I_2]= 5.5mmol/l, [KI]=16.7mmol/l, 6-8 °C, 20hrs.

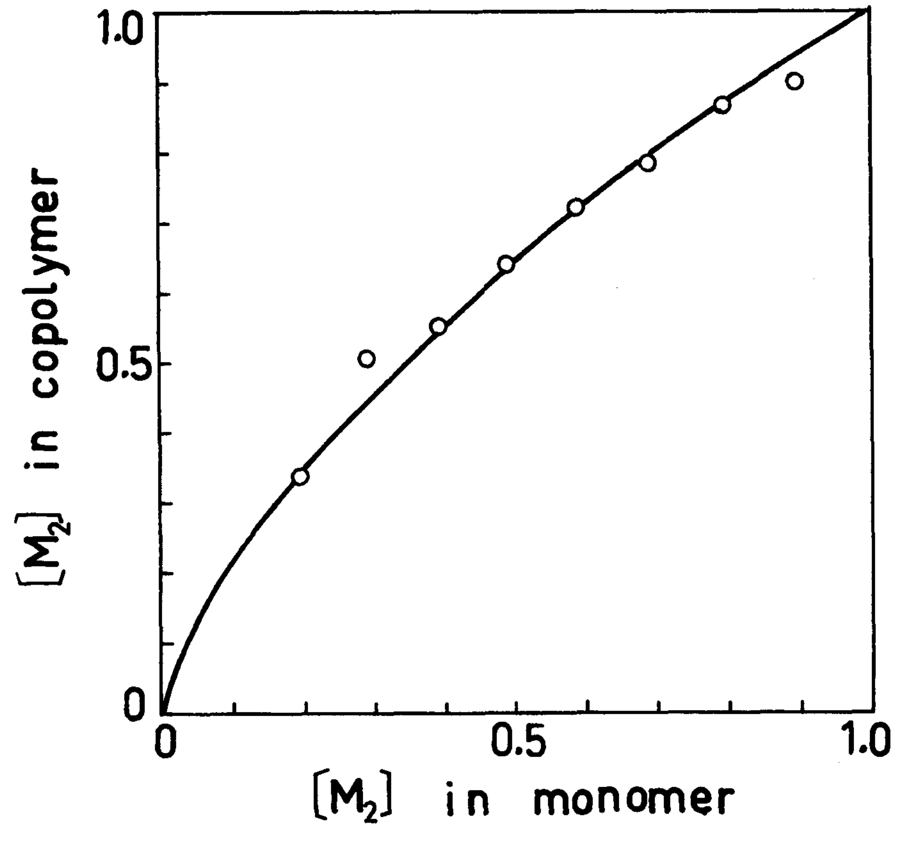

Figure 1. Copolymer composition curve for vinyl acetate(M_1) and divinyl carbonate(M_2)
: $[M_1]+[M_2]=2$ mol/l in methanol at 1°C; catalyst, $(i\text{-Bu})_3B$ o.33 mol% of monomer; the curve is calculated for $r_1=0.41$, $r_2=1.55$

Discussion

Effect of the 1,2-Glycol Structure on the PVA-Iodine Reaction

The increase of 1,2-glycol content, as shown in Figure 2, strongly influences the PVA-iodine reaction. Particularly when the 1,2-glycol contents are larger than 5mol%, the reaction mixtures are colorless. The PVA samples are almost identical to one another with respect to stereoregularity and the degree of polymerization. Therefore, the decrease of the intensity of visible absorption (coloring ability) solely depends on the increase of the 1,2-glycol content. Further, the fact that absorption maxima are unchanged independent of the 1,2-glycol content suggests that the structures of the PVA-iodine complexes are identical to one another.

Table II shows that the IR absorbance ratios, D_{916}/D_{849}, decrease as the 1,2-glycol contents decrease. The values of D_{916}/D_{849}, however, may not reflect the stereoregularity of PVA when PVA has a large 1,2-glycol content as informed earlier$^{5)}$. The polymerization conditions suggest these PVA samples to be atactic.

We have previously reported that the 1,2-glycol structure is one of important factors which interfere with the crystallization of PVA. The influence of the 1,2-glycol structure in the present report differs from that on the crystallization. Figrue 3 shows that the melting point of PVA inversely corresponds to the 1,2-glycol content when the contents are less than 13mol%$^{5)}$.

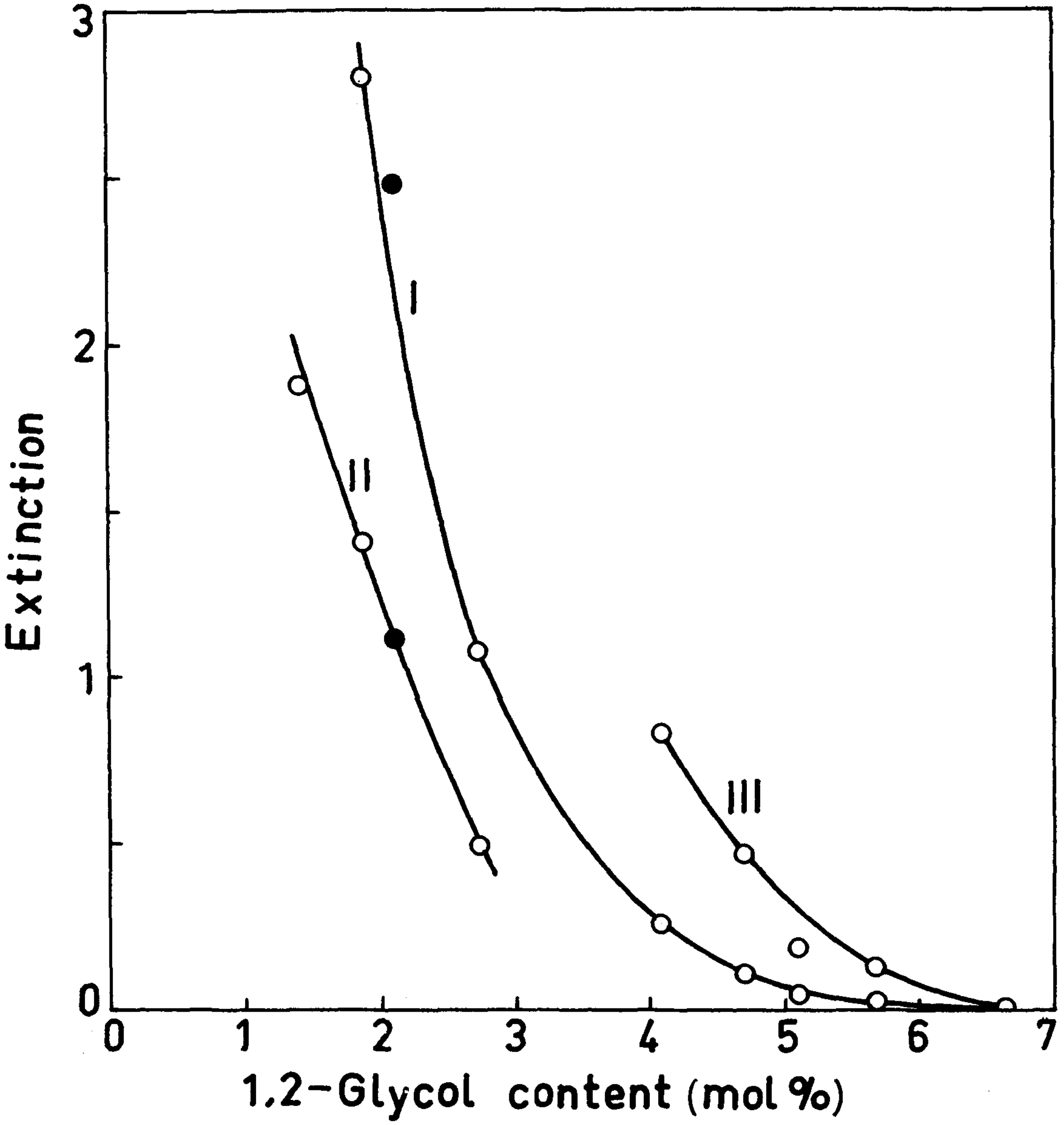

Figure 2. Effect of 1,2-glycol on PVA-iodine reaction

○ : Samples from the vinyl acetate-divinyl carbonate copolymer

● : Commercial PVA

Reaction conditions for I, II, and III are listed in Table I.

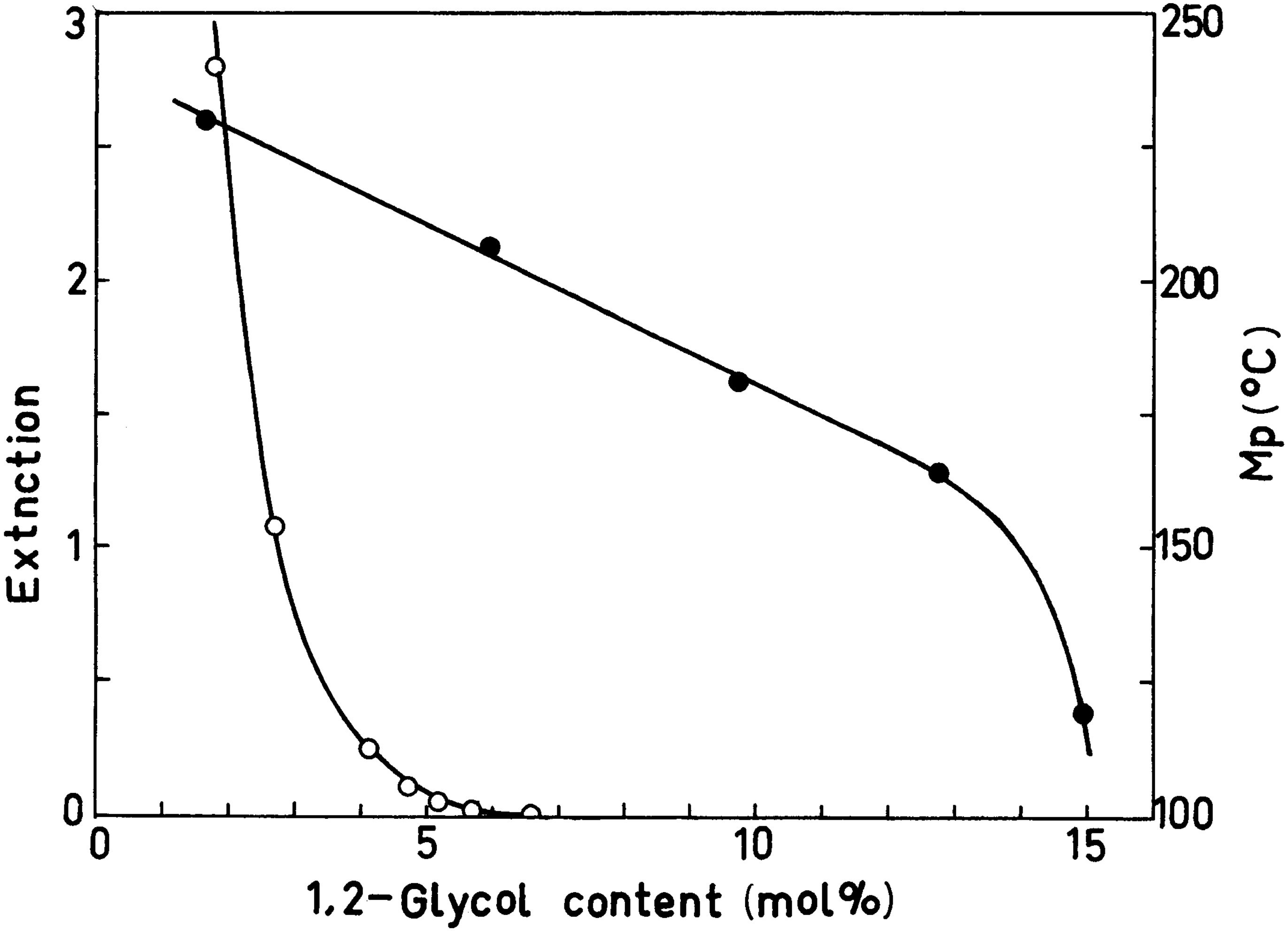

Figure 3. Effect of 1,2-glycol structure on PVA-iodine reaction (○) and on melting point of PVA(●)

Whereas the PVA-iodine reaction suffers a large effect from much smaller amount of the 1,2-glycol content. This tendency was remarkable at a reaction temperature of 20°C which was employed by Shibatani and others4). The difference in these two properties suggests that the PVA-iodine reaction requires a longer 1,3-glycol sequence length than does the crystallization of PVA.

Let us assume that a sequence length n of 1,3-glycol units is required for the color reaction. If one assumes that the 1,2-glycol units are distributed statistically along the chain, the probability of the occurrence of sequence length x of 1,3-glycol units is obtained approximately by the formula,

$$P(x) = \left(\frac{a+1}{N}\right)\left(\frac{b-1}{N}\right)^{x} \qquad (1)$$

where N is degree of polymerization, a and b are average numbers of 1,2- and 1,3-glycol units in polymer molecules, respectively, that is $a+b=N$. Therefore the mole fraction of the 1,3-glycol units which are contained in sequences with more than n, f(n), is obtained by the formula,

$$f(n) = 1 - \frac{\sum_{x=1}^{n} xP(x)dx}{\sum_{x=1}^{\infty} xP(x)dx} \qquad (2)$$

Combination of Eq.1 and Eq.2 gives Eq.3, which can be calculated assuming various n values.

$$f(n) = \left(\frac{b-1}{N}\right)^{n-1} \left(\frac{n - 1/\ln\left(\frac{b-1}{N}\right)}{1 - 1/\ln\left(\frac{b-1}{N}\right)}\right) \qquad (3)$$

Table VII shows the mole fraction of the 1,3-glycol units with

Table VII. Mole fraction of the 1,3-glycol units contained in sequences of more than n.

The values in parentheses are relative values taking No.3 as a standard.

Sample No.	D_{max}	n=100	n=120	n=150
1	-	0.522(2.92)	0.425(3.83)	0.305(5.87)
2	2.8(2.6)	0.378(2.11)	0.279(2.52)	0.174(3.35)
3	1.08(1.00)	0.179(1.00)	0.111(1.00)	0.052(1.00)
5	0.26(0.24)	0.046(0.25)	0.020(0.18)	0.0056(0.11)
6	0.11(0.10)	0.024(0.14)	0.0091(0.082)	0.0021(0.040)
7	0.048(0.045)	0.015(0.083)	0.0051(0.046)	0.00098(0.019)
8	0.026(0.024)	0.0073(0.041)	0.0023(0.021)	0.00035(0.007)
10	0.009(0.008)	0.0022(0.012)	0.0005(0.004)	0.00005(0.0009)

n=100, 120 and 150 in the PVAs of different 1,2-glycol content. In order to facilitate a comparison between the observed extinction and the calculated value, sample No.3 was taken as a standard. In Figure 4, curves represent relations between the calculated relative amount of the 1,3-glycol units contained in sequences of more than n and the 1,2-glycol content, showing a good correspondence between the observed and the calculated value when n=120. Namely, the conditions of the PVA-iodine reaction supposingly require an extremely long 1,3-glycol sequence length of atactic configuration. The value of 120 in 1,3-glycol sequence length obtained here does not directly relate to the PVA-iodine complex, because other factor than the 1,2-glycol structure may influence the PVA-iodine reaction. Thus an extremely long sequence length may be necessary in case of the atactic PVA. Indeed, syndiotactic PVA has high coloring ability in spite of low degree of polymerization4).

In order to check the effect of vicinal arrangement of hydroxyl groups, a comparison between the influence of the 1,2,3-triol structure on the PVA-iodine reaction (closed circle) and that of 1,2-glycol (open circle) was made in Figure 5. This figure indicates that the effect of the 1,2-glycol structure inevitably gives the 1,4-glycol structure and both the structures probably infavor the color reaction, while the 1,2,3-triol structure does not give the 1,4-glycol structure. Thus it is not the vicinal arrangement of OH groups but the structural irregularity that influences the color reaction. Shibatani et al.

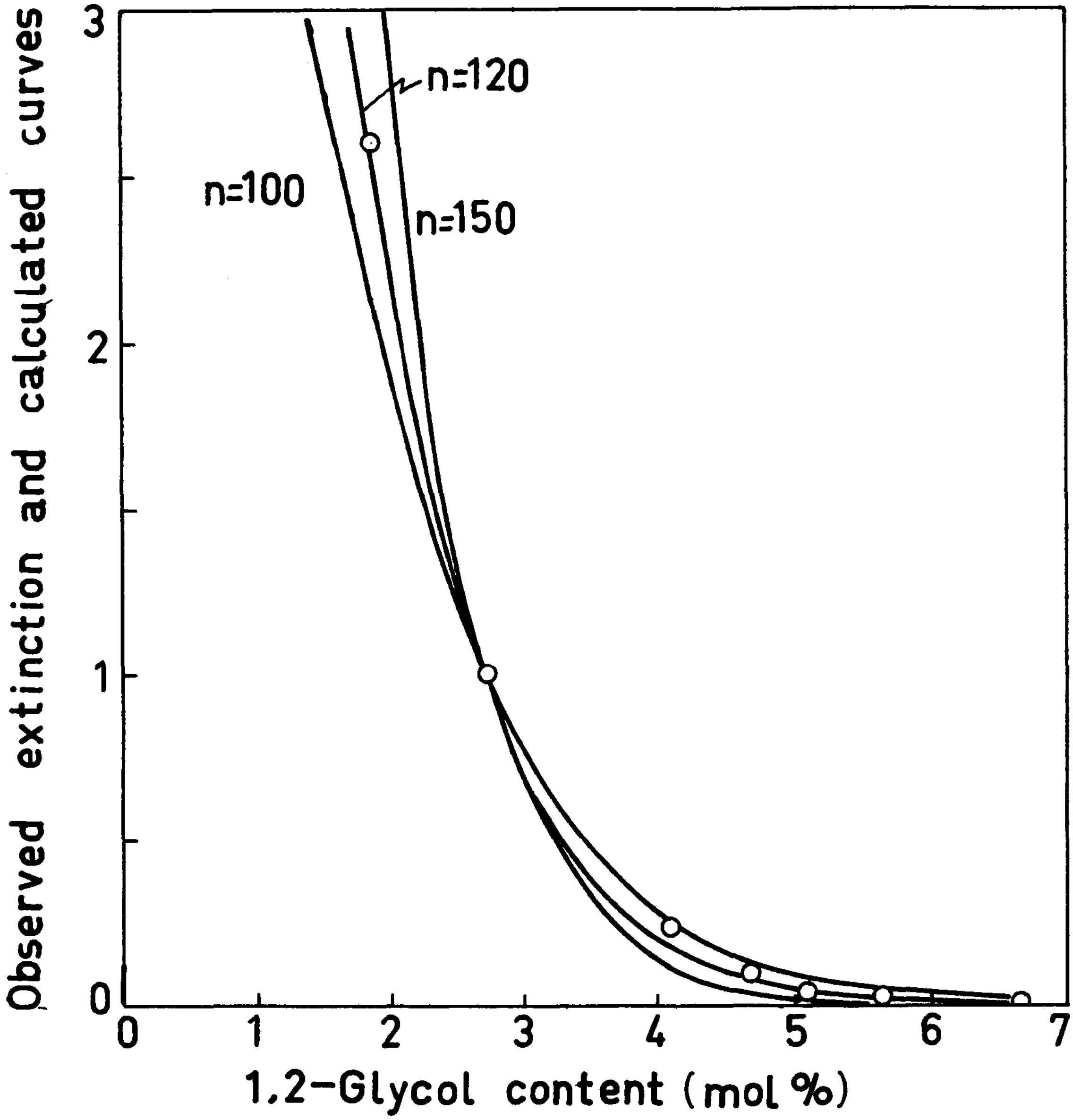

Figure 4. Relation between the calculated relative amounts of the 1,3-glycol uniys contained in sequences of more than n and the 1,2-glycol content. Curves represent the calculated values and circles the observed values.

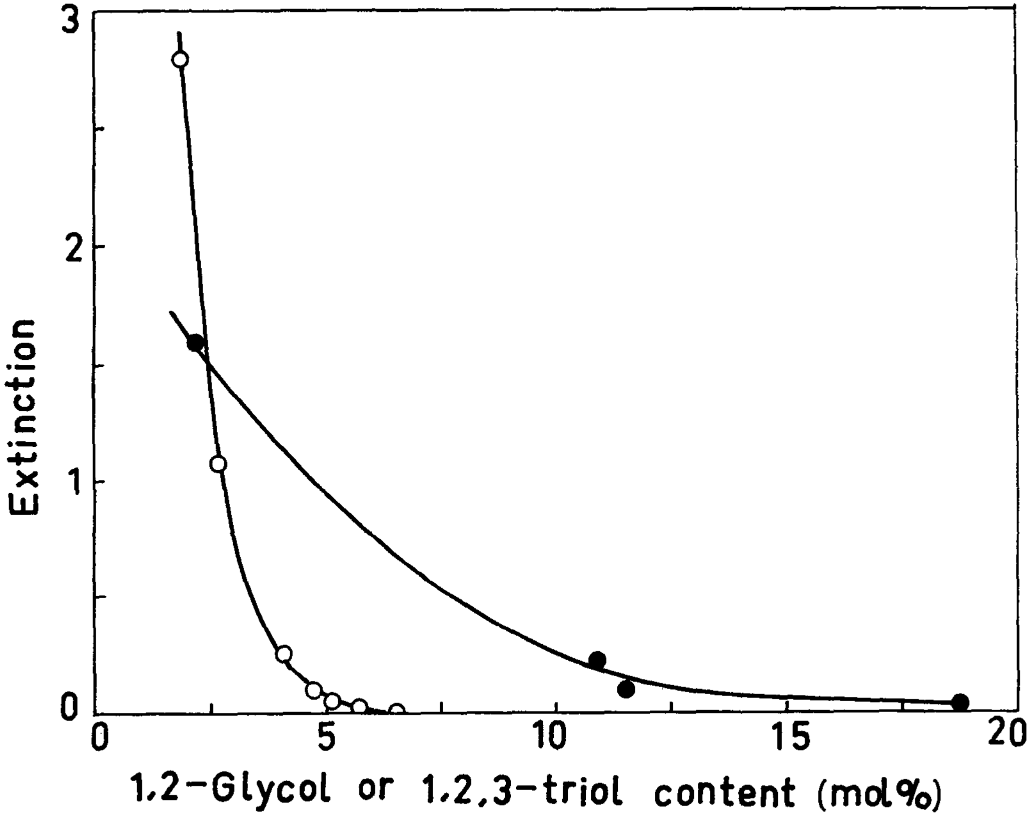

Figure 5. Effect of 1,2,3-triol structure on PVA-iodine reaction

● : Effect of 1,2,3-triol structure. [PVA]=25mmol/l, $[I_2]$=1.25 mmol/l, [KI]=2.5 mmol/l, 6-8°C, 20 hrs.

○ : Effect of 1,2-glycol structure. [PVA]=30 mmol/l, other conditions are the same as above.

have carried out a similar experiment and failed to obtain a difference between the 1,2-glycol and 1,2,3-triol structures$^{4)}$. It is conceivable that, as compared to our experiment, the reaction temperature was high and so the formation of the PVA-iodine complex was more difficult.

The Effect of the Stereoregularity on the PVA-Iodine Reaction

PVA samples (No.21-30) derived from vinyl trimethylsilyl ether are known to contain negligibly small amount of 1,2-glycol unit$^{1)}$. The influence of stereoregularity on the PVA-iodine reaction is also remarkable. The results in Tables V and VI show that PVA with syndiotacticity larger than 50% showed high coloring ability and PVA samples with syndiotacticity less than 30% do not show the color reaction. It is characteristic to PVA samples with syndiotacticity of about 40% that the increase in the isotactic structure results in the shift of the absorption maximum as well as the decrease in extinction. This fact is in contrast with the effect of the 1,2-glycol structure on the PVA-iodine reaction, and suggests that the effect of stereoregularity may be different qualitatively from that of the 1,2-glycol structure, that is, the isotactic structure may have an influence on the structure of the PVA-iodine complex. The tendency of the isotactic PVA to form an intramolecular hydrogen bonding$^{8)}$ may reflect on the PVA-iodine reaction.

The similarity of the PVA-iodine reaction to the amylose-iodine reaction suggests that the blue color may be due to the interaction between polyiodine, I_n^{m-}, and oxygen atoms of surrounding PVA chains [9,10,11]. The structure and the amount of the site which stabilizes polyiodine may change the absorption maximum and extinction. In case of the amylose-iodine reaction, this structure is determined as a helix; in case of the PVA-iodine reaction it is not clear although a helical structure was suggested by Zwick[10].

Imai et al.[3] and Shibatani et al.[4] have shown that the PVA-iodine reaction has a close relation with the intermolecular interaction of PVA. Since an isotactic sequence interferes with the formation of the intermolecular hydrogen bonding, a blue shift of the absorption maximum with increasing isotacticity may be due to the fact that intramolecular hydrogen bonding reduces the interaction between polyiodine and oxygen atoms of PVA. But the sequence length forming an intramolecular hydrogen bonding is not so long to destroy the complex completely at these medium isotacticity.

The addition of boric acid generally promotes the PVA-iodine reaction and shifts the absorption maximum to a longer wave length(670-700mμ). Boric acid may intensify the intermolecular interaction of PVA and consequently may promote the interaction between PVA and iodine. Without boric acid, the color reaction was not observed on samples No.21 and 22. The addition of boric acid to these developed the color, but the visible absorptions are too broad to determine the absorption maximum. It is interesting to note that a sample which is rich in isotactic structure(No.21, 88% isotacticity) was colored more intensely than No.22(80% isotacticity). Sample No.21 is less soluble in water than No.22, which is the most soluble among various tacticities, and some other kind of intermolecular interaction than hydrogen bonding was suggested 1). The intermolecular interaction is reinforced by boric acid probably at the segments not having intramolecular hydrogen bondings, resulting in the formation of the PVA-iodine complex. The broad absorption spectrum also suggests that this interaction may not be so simple as the interaction in atactic or syndiotactic PVA.

The comparison between the influence of stereoregularity on the PVA-iodine reaction and that of the 1,2-glycol structure is summed up as follows: the existence of 1,2-glycol structure discontinues the interaction between PVA and iodine, but does not influence the structure of PVA-iodine complex. The isotactic structure may modify the structure of the PVA-iodine complex so as to weaken the interaction, finally entirely suppressing the complex formation at isotacticity higher than 70%.

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Chapter III

Poly(vinyl alcohol)-Iodine Reaction of Poly(vinyl alcohol) fractionated by Foaming

Synopsis

It has been confirmed that foam fractionation of an aqueous poly(vinyl alcohol) solution produced poly(vinyl alcohols) with different reactivity on the poly(vinyl alcohol)-iodine reaction, namely the color intensity decreased with increase in the fraction number. This result was found not only with a poly(vinyl alcohol) derived from poly(vinyl acetate), but also with a specimen derived from cationically polymerized poly(vinyl trimethylsilyl ether). Particularly in the case of poly(vinyl alcohol) obtained from poly(vinyl acetate)(degree of polymerization = 1652, syndiotacticity = 50.0% in diad), the variation of color intensity among the fractions can not be explained by any one of the structural factors such as molecular weight, the 1,2-glycol structure, stereoregularity, and the carbonyl group in the main chain. Therefore an other molecular structure, for example short branching, which will affect the poly(vinyl alcohol)-iodine reaction and the foam fractionation should be considered.

The result also indicates the homogeneity of poly(vinyl alcohol) from poly(vinyl acetate) with respect to stereoregularity and the 1,2-glycol structure contents. In the case of poly(vinyl alcohol) obtained from poly(vinyl trimethylsilyl ether) (degree of polymerization = 1496, syndiotacticity = 37.5% in diad), the fractionation with respect to stereoregularity has occurred: syndiotacticity of poly(vinyl alcohol) contaned in foam layers was higher than that in the residual solution. This result indicates that the poly(vinyl alcohol) derived from poly(vinyl trimethylsilyl ether) consisted of stereoblock and/or a mixture of poly(vinyl alcohol) of different tacticity.

Introduction

Imai et al. sepatated a poly(vinyl alcohol)(PVA) derived from radically polymerized poly(vinyl acetate)(PVAc) into fractions by foaming an aqueous solution1). The fractions showed different reactivity in the PVA-iodine reaction though there is little difference in degree of polymerization and in the 1,2-glycol content. They suggested that PVA was fractionated according to stereoregularity. But there arises a question in considering the presence of wide difference of stereoregularity among individual polymer molecules of a radical polymer.

It is known that even a minor change in molecular structure

Of PVA influences the properties of PVA. Factors, which may affect crystallinity and PVA-iodine reaction, involve the 1,2-glycol structure, the carbonyl group in the main chain, branching and stereoregularity. Since the method of determination of stereoregularity was established2), PVA samples with different stereoregularities have been prepared in order to study the effect of stereoregularity on properties of PVA3). The increase of isotacticity of PVA loweres melting point, crystallinity, and color intensity of the PVA-iodine reaction3,4,5). Murahashi et al. showed that the increase of the 1,2-glycol structure deteriorates the crystallinity4) and fades the color of the PVA-iodine reaction5). In addition, Shibatani et al. have shown that a minor change in 1,2-glycol contents remarkably affects the PVA-iodine color reaction6).

This work was undertaken to investigate the properties of PVA fractionated by foaming in detail, and to elucidate the effect of the change in the molecular structure of PVA on the PVA-iodine reaction and on the foam fractionation. Foam fractionation of PVA derived from cationically polymerized poly(vinyl trimethylsilyl ether)(poly(VOSi)) which was nearly atactic, was also investigated.

Experimental

PVA Samples

Sample A was a commericial PVA(Kuraray Co., Ltd.) which was derived from radically polymerized PVAc. Degree of polymerization =1652, residual acetate group = 0.23%, sodium acetate = 0.25%, syndiotacticity = 50.0% in diad, the 1,2-glycol content = 2.12%.

Sample B was prepared by methanolysis of a poly(VOSi) prepared from the cationic polymerization of VOSi. The polymerization procedure was as follows: a mixture of 200ml of VOSi, 1000ml of methylene chloride, and 800ml of toluene was placed in a 2l three-necked flask under a nitrogen atomosphere, the flask was then cooled to -70 °C with a dry ice-methanol bath. When ethylaluminum dichloride(0.7ml) was added slowly to the flask under stirring, the reaction temperature rose temporally to -50 °C, and then the solution was stirred for two hours at -70 °C. The polymerization mixture was poured into a large amount of methanol. Methanolysis of the resulting polymer and precipitation of PVA occurred simultaneously. The PVA was washed several times with methanol by decantation and separated by filtration and dried under vacuum. Yield was 52.0g(91%). Degree of polymerization = 1496, syndiotacticity = 37.5% in diad, the 1,2-glycol content=0.25%.

Foam Fractionation

Sample A: a solution of 60g of PVA and 3l of water was placed in a 5l wide-mouthed bottle. The bottle was shaken at a frequency of 68cycle per minute: a foam layer was thus created. After being shaken for apropriate period, the soultion was allowed to stand for a certain time. In the course of this standing, part of the foam usually disintegrated and the remaining foam layer was taken out as a foam cake. The residual solution was usually cloudy, and there was a slight amount of precipitate at the bottom of the bottle. To obtain successive fractions, the cloudy solution was heated until it became completely clear and then the procedure involving shaking, standing, separation and heating was repeated.

Sample B: fractionation procedure was the same as the above except for the use of 40g of PVA and 2l of water.

PVA-Iodine Color Reaction

An aqueous PVA solution was mixed with a KI-I_2 solution at 6~8 °C and kept at this temperature for 23hrs. The mixture was subjected to spectroscopic measurement at room temperature using a Hitachi spectrophotometer, EPS-3T.

Sample A: $[PVA]=15 mmol/l$, $[I_2]=1.25 mmol/l$, $[KI]=5 mmol/l$.

Sample B: $[PVA]=30 mmol/l$, $[I_2]=1.25 mmol/l$, $[KI]=5 mmol/l$.

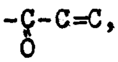
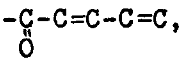
Characterization of PVA

Degree of polymerization of PVA was calculated from viscosity of 1% aqueous PVA solution at 30 °C according to the equation presented by Nakajima et al7).

Diad syndiotacticity of PVA was calculated from the absorbance ratio, D_{916}/D_{849}, of the IR spectra of PVA films, which was prepared from 1% aqueous solution and dried at 30°C in a silica gel desiccator, according to the following equation presented by Murahashi et al.2)

$$s(\text{diad})\% = 72.4(D_{916}/D_{849})^{0.43}$$

The content of 1,2-glycol structure was determined by titrating the periodic acid consumption by PVA in accordance with the method of Harris et al.8) In the case of Sample B, the content was also determined by degree of polymerization of PVA oxydized by periodic acid in accordance with the method of Flory9).

The carbonyl group in main chain was measure by the UV spectra of aqueous PVA solutions. Absorption maxima at 240mμ and 280mμ are assighned to  $-\underset{\overset{\|}{O}}{C}-C{=}C$, and  $-\underset{\overset{\|}{O}}{C}-C{=}C-C{=}C$, respectively10).

Results

The results of foam fractionation of Sample A and Sample B are given in Table I and II, reaspectively. Sample A produced stable foams and thus gave a large number of fractions, whereas Sample B produced less stable foams and most of the sample remained in solution. The change of the various properties of PVA according to the fractionation are given in Table III and IV.

Table I. Foam fractionation of Sample A

Fraction No.	Shaking time, hr,	Standing time, hr,	Yield g,	Yield %,
A 1	18	5	3.09	5.15
A 2	18	5	3.77	6.28
A 3	18	5	3.68	6.13
A 4	21	24	3.72	6.20
A 5	21	24	4.25	7.08
A 6	21	24	3.72	6.20
A 7	23	24	2.84	4.73
A 8	21	24	3.58	5.97
A 9	21	24	1.85	3.08
A 10	21	24	2.26	3.77
A 11	24	45	1.42	2.37
A 12	24	45	1.52	2.53
A 13	24	45	1.09	1.82
A 14	24	45	0.85	1.42
A 15	24	45	0.61	1.02
A 16	24	45	0.57	0.95
A 17	24	45	0.74	1.23
A 18	24	45	0.56	0.93
A-R[a)]	-	-	16.90	28.17

a) Residual PVA in solution

Table II. Foam fractionation of Sample B

Fraction No.	Shaking time, hr,	Standing time, hr,	Yield g,	Yield %,
B 1	10	24	0.308	0.91
B 2	20	48	1.030	2.56
B 3	20	24	0.890	2.21
B 4	20	24	0.599	1.48
B 5	20	48	0.503	1.25
B 6	20	24	0.320	0.79
B 7	20	24	0.402	1.00
B 8	20	24	0.308	0.76
B 9	20	24	0.240	0.69
B 10	20	48	0.111	0.27
B 11	20	48	0.245	0.60
B 12	20	48	0.126	0.31
B-R^a)	-	-	35.24	88.0

a) Residual PVA in solution

Table III. Structure and Properties of Foam-fractionated Sample A

Fraction No.	DP	Syndiotacticity, %,	1,2-glycol mol%,	UV spectra[a]	PVA-I_2 reaction[b]	
				d_{230}	d_{max}	λ_{max}, mμ,
A 0[c]	1652	50.0	2.12	-	1.79	614
A 1	2060	53.0	2.14	2.5	3.23	"
A 2	1974	50.0	-	1.8	3.28	"
A 3	1991	50.0	-	2.7	3.07	"
A 4	2349	50.5	2.07	1.9	3.30	"
A 5	2384	51.0	-	1.3	3.20	"
A 6	2256	51.5	-	1.5	2.87	"
A 7	2371	52.0	2.03	0.77	2.70	"
A 8	2509	49.0	-	0.72	2.47	"
A 9	2173	51.0	-	0.94	2.13	"
A 10	2193	50.0	2.00	0.71	1.96	"
A 11	1879	49.0	-	0.83	1.51	"
A 12	-	49.5	-	0.86	1.07	"
A 13	1524	49.0	1.98	0.85	0.84	"
A 14	1583	49.5	-	1.4	0.79	"
A 15	1571	48.5	-	0.61	0.76	"
A 16	1490	49.0	2.05	-	0.44	"
A 17	1450	49.0	-	0.51	0.40	"
A 18	1168	48.5	-	-	0.31	"
A-R[d]	743	48.5	2.13	-	0.06	"

a) Aqueous PVA solution(0.6%), λ_{max}=230mμ

b) Reaction conditions; [PVA]=15mmol/l, [I_2]=1.25mmol/l, [KI]=5mmol/l at 6~8°C for 23hrs

c) Original unfractionated PVA

d) Residual PVA in solution

Table IV. Structure and Properties of Foam-fractionated Sample B

Fraction No.	DP	Syndiotacticity, %	1,2-glycol mol%	UV spectra[a]	PVA-I_2 reaction[b]	
				d_{240}	d_{max}	λ_{max}, mμ
B 0[c]	1496	37.5	0.25[e], 0.35[f]	-	0.216	596
B 1	1449	43.5	-	2.62	1.542	602
B 2	1577	44.0	0.14, 0.1	-	1.484	602
B 3	1578	41.5	-	1.10	1.411	605
B 4	1520	44.0	-	1.91	1.352	606
B 5	1585	41.5	- , 0.50	0.82	1.159	606
B 6	1572	42.5	-	0.98	1.081	606
B 7	1542	44.0	-	1.33	0.753	608
B 8	1554	42.5	-	0.84	0.735	606
B 9	1513	41.5	-	0.74	0.674	606
B 10	1522	42.0	-	0.96	0.953	605
B 11	1431	41.5	-	0.83	0.383	601
B 12	1424	41.0	-	0.80	0.413	597
B-R[d]	1490	38.0	0.40, 0.58	-	0.433	562

a) Aqueous PVA solution(0.6%), λ_{max}=240m

b) Reaction conditions; [PVA]=30mmol/l, [I_2]=1.25mmol/l, [KI]=5mmol/l at 6~8°C for 23hrs

c) Original unfractionated PVA

d) Residual PVA in solution

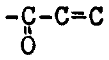
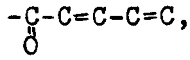
e) Determined by the viscometric method

f) Determined by the periodate method

Figure 1 shows that the degree of polymerization of Sample A in each fraction was not constant but increased slightly with an increase in the fraction number and then decreased. On the other hand, the degree of polymerization of Sample B in each fraction was substantially constant.

There is little defference in the 1,2-glycol structure content of Sample A(Table III) and B(Table IV) in each fraction and a systematic change was not found.

As may be seen in Figure 2, the stereoregularity of Sample A in each fraction essentially unaltered within the experimental error and was the same as that of the original PVA. The syndiotacticity of Sample B contained in the foam layer is higher than that of the original PVA. Therefore Sample B was separated according to syndiotacticity, but there was not systematic change of stereoregularity among fractions.

The aqueous solutions of Sample A and Sample B exhibit their absorption maxima at about 230mμ(Sample A), 240mμ(Sample B) and 280mμ(weak), which were assigned to  $-\underset{\overset{\|}{O}}{C}-C=C$ and  $-\underset{\overset{\|}{O}}{C}-C=C-C=C$, respectively(Table III and IV)$^{10)}$. The relationship between the absorbance at 230mμ(240mμ for Sample B) and the fraction number is depicted in Figure 3; there is no clear-cut dependence of the absorbance on the fraction number though the early fractions tend to absorb more intensely than the later fractions.

The intensity of the PVA-iodine color reaction(d_{max}) of Sample A and Sample B is shown in Figure 4. Systematic changes

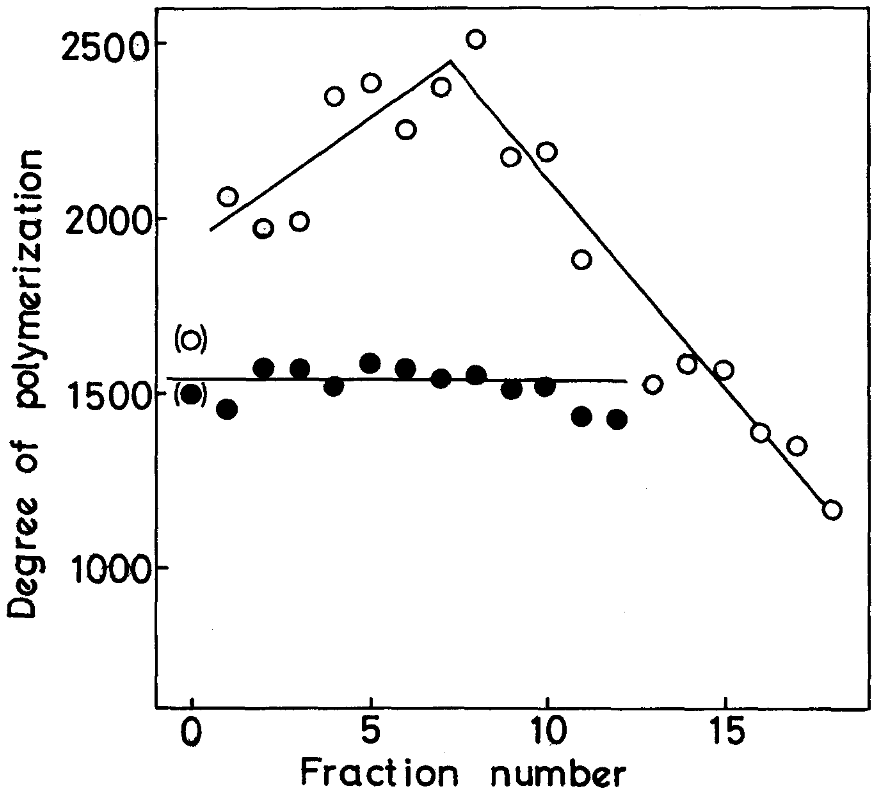


Figure 1. Degree of Polymerization of Fractions

○; Sample A

●; Sample B

Plots in parentheses represent the original PVA

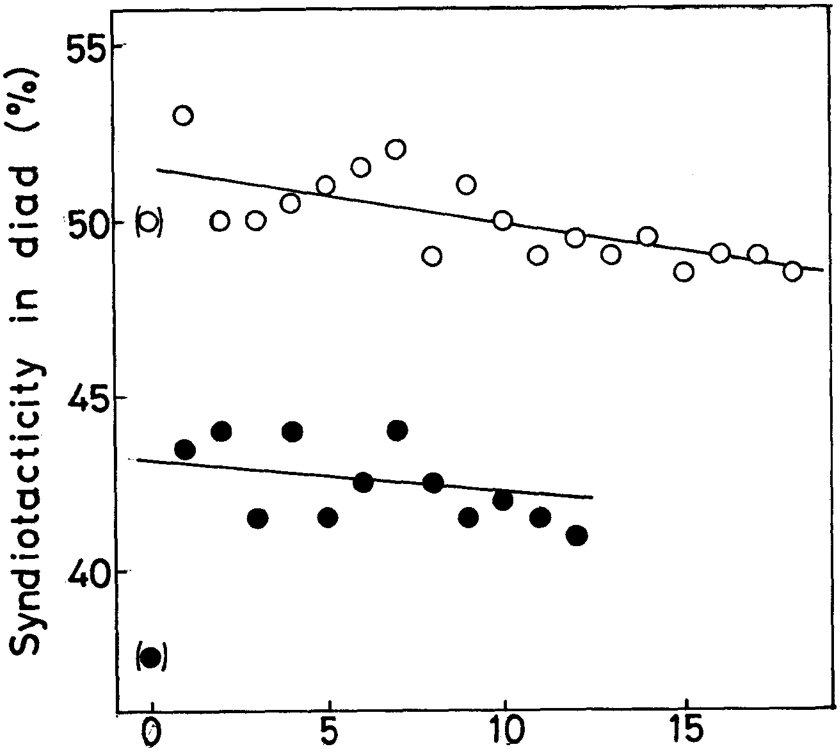


Figure 2. Stereoregularity of Fractions

○ ; Sample A

● ; Sample B

Plots in parentheses represent the original PVA

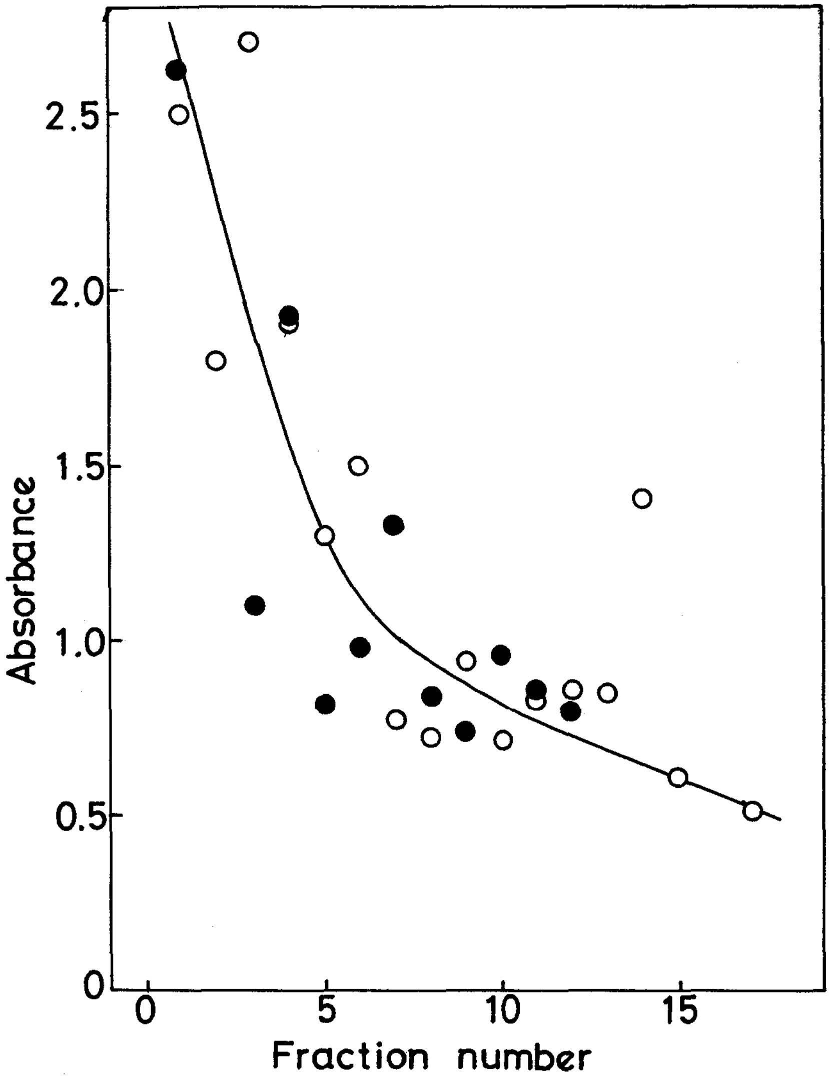


Figure 3. Absorbance at 230mμ(Sample A) and 240mμ (Sample B) of Aqueous Solution of Fractions

○; Sample A

●; Sample B

[PVA]=0.6% in water

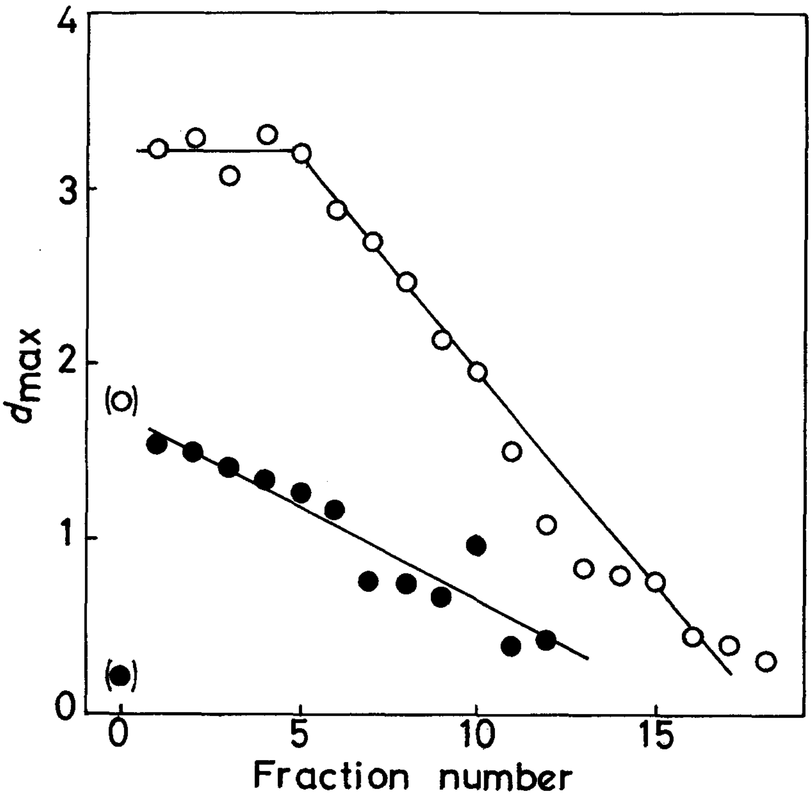


Figure 4. The Iodine-Color Reaction of Fractions

○; Sample A, [PVA]=15mmol/l, $[I_2]$=1.25mmol/l, [KI]=5mmol/l, 6～8 °C, 23hrs

●; Sample B, [PVA]=30mmol/l, other conditions are the same as sample A

Plots in parentheses represent the original PVA.

of d_{max} of Sample A and B in each fraction was clearly found, that is, as the fractionation progresses, d_{max} decreases remarkably. It is characteristic to Sample B that the absorption maxima varied with fraction number as shown in Table IV.

Discussion

Foam fractionation in low molecular weight compounds takes advantage of adsorption of surface-active agents on interface and have found wide applications11). In the case of high molecular weight compounds such as protein, starch and synthetic high polymer, the foam is stabilized by the formation of films of a gel-like substance12). Viscosity of the solution also affects the stability of the foam. In the case of the solution of PVA, the formation of remarkably stable foam will suggest the gelation. Therefore the foam fractionation described here may be similar in principle to the mechanical denaturation of PVA solution reported by Go et al.13) The above discussion suggests the possibility of the fractionation of PVA according to the molecular structure, which influence the tendency of gelation, such as stereoregularity, the 1,2-glycol content, the carbonyl group and branching.

As may be seen in Table III, IV and Figure 4, a characteristic result in the foam fractionation of a PVA solution was a decrease of the PVA-iodine color with an increase of fraction number. The PVA-iodine color reaction is strongly affected by molecular weight, stereoregularity, the 1,2-glycol structure of PVA as reported previously. The color reaction is also reported to correspond to the degree of swelling of PVA, which probably reflects the crystallinity.

Figure 1 shows that the degree of polymerization of Sample A is not constant but increase with an increase in the fraction number and then decrease, whereas that of Sample B is essentially constant, that is, the fractionation did not occur with respect to molecular weight. Imai et al. reported a linear relationship between the intensity of the PVA-iodine color and the degree of polymerization of fractionated PVA, $D_{620} \propto DP$[14]. A relationship between d_{max} corrected for molecular weight by the above equation (d_{max} was used instead of D_{620}) and the fraction number are shown in Figure 5. The data of Sample B in Figure 5 were converted to a concentration of 15mmol/l of PVA in order to compare directly with data of Sample A. The linear relationship between the corrected d_{max} and the fraction number also indicates that molecular weight is not main factor of the change of d_{max}.

The 1,2-glycol content of the fractions was almost constant, hence the fractionation with respect to the 1,2-glycol content did not occur, and the 1,2-glycol content can not explain the decrease of the color. This result does not deny the possibility of foam fractionation according to the 1,2-glycol structure of

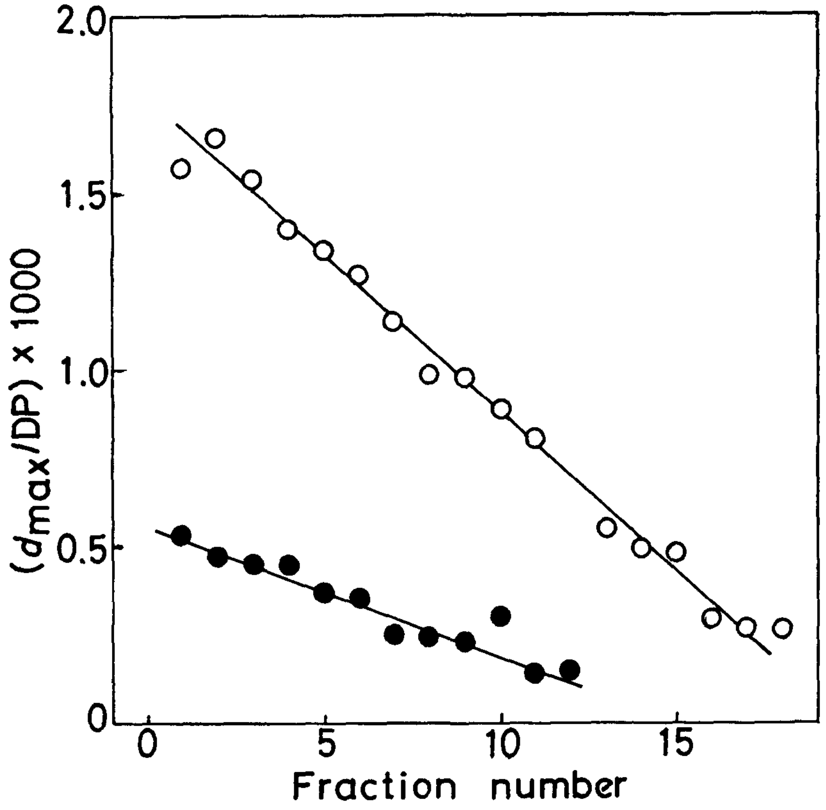


Figure 5. Corrected Absorbance for the Iodine-Color Reaction of Fractions

○; Sample A

●; Sample B, The data of Sample B were converted to 15mmol/l PVA concentration

PVA in general but represents the homogeneity of the PVA specimens.

Figure 2 shows that tacticity of the fractions of Sample A was nearly equall to each other and to that of the original PVA. Since Sample A is obtained from radically polymerized PVAc, the sequence of stereoregularity probably follows random distribution. Thus an appreciable difference should not be present concerning stereoregularity among individual polymer molecules and hence each fractions. The constancy of absorption maximum in the I_2 color reaction also represents the homogeneity of the tacticity of Sample A5). Then, the decrease of d_{max} at Sample A with the increase of fraction number can not be explained by stereoregularity

On the other hand, the syndiotacticity of the fractions of Sample B was higher than that of the original PVA, and the foam was unstable and the yield of foam was low compared with Sample A though a difference in tacticity among the fractions was not found. This results suggest that a considerable syndiotacticity is necessary for producing a stable foam and that the foam franctionation with respect to stereoregularity has occurred for Sample B. A large hypsochromic shift of absorption maximum of Sample B with fraction numbers(Table IV) also shows the fractionation with respect to stereoregularity because an isotactic PVA shows the hypsochromic shift at the PVA-iodine color reaction5). Sample B is probably heterogeneous with respect to stereoregularity15). The high conversion and the elevation of temperature at the beginning of the polymerization may be one of the reason for the production of the polymer molecules with different stereoregularity. In contrast, a successive change of tacticity was not found among the foam fractions as shown in Figure 2. The d_{max} of the fractions, however, decreased with the increase of the fraction number, though the difference in this case was smaller than that in the case of Sample A(Figure 5). The d_{max} of Sample B of the residual solution was more intense than that of original PVA but these d_{max} might not be directly compared with because of the large difference of λ_{max}. Figure 6 shows the plots of the corrected d_{max} against syndiotacticity; these plots also shows that the gradual decrease of d_{max} does not correlate with stereoregularity. Namely the stereoregularity is not a main factor govering the difference of the color reaction of PVA among the fractions.

Go et al. reported that a mechanical stirring of an aqueous PVA solution yielded precipitates of PVA with different color intensity of the PVA-iodine reaction in spite of the same syndiotacticity as that of the original PVA$^{13)}$. They suggest that the difference of sequence length of syndiotactic part of each PVA is not the same. This suggestion, however, may not be reasonable in the present case because the PVA obtained by radical polymerization may consist of random sequence distribution of stereoregularity and the difference between polymer molecules is probably small.

The presence of carbonyl group in the main chain is revealed

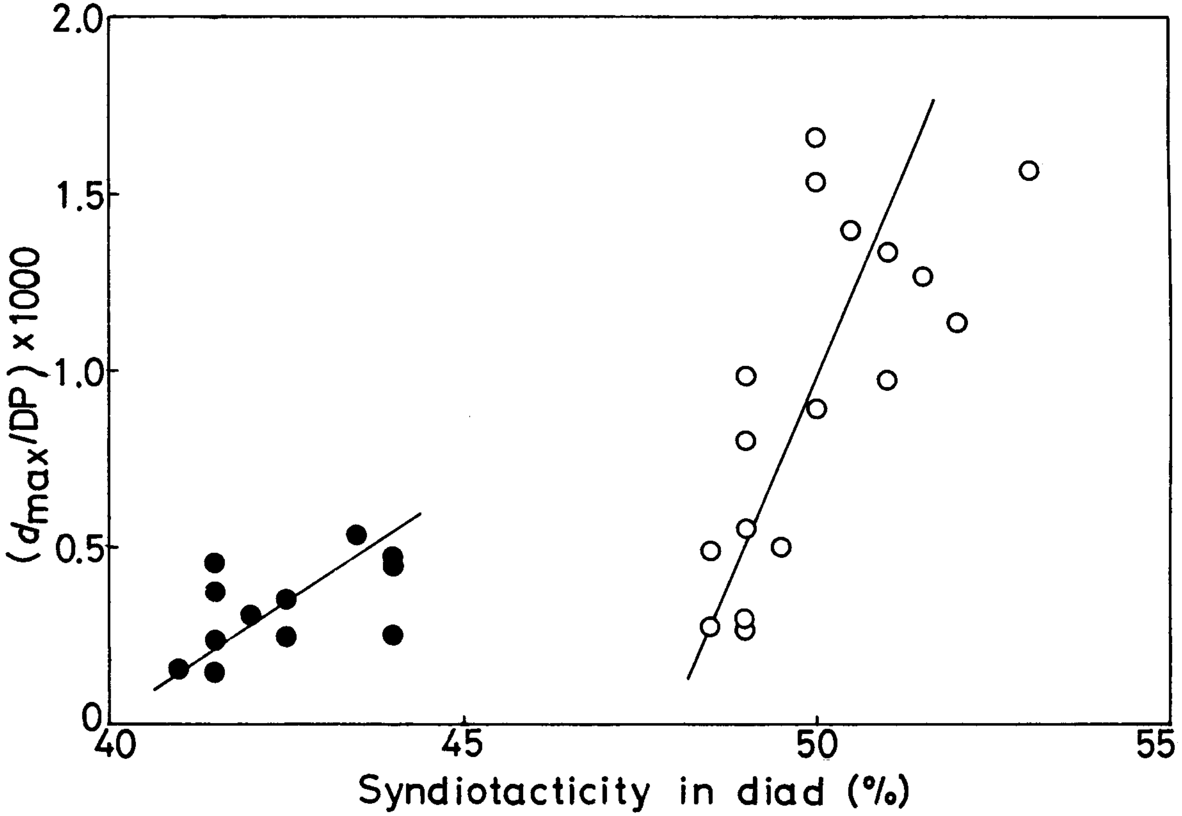


Figure 6. Relation between the Iodine-Color Reaction and Tacticity

○ ; Sample A, ● ; Sample B

by the absorption maximum at 230mμ(Sample A), 240mμ(Sample B) and 280mμ. Figure 3 shows the plots of the absorbance of 230mμ and 240mμ, which have been assigned to the $-\underset{\overset{\|}{O}}{C}-C=C$ structure, against the fraction number. Roughly speaking the early fractions tend to show stronger absorptions. These results disagree with the conventional information that the presence of abnormal structures disturbs the gelation and the PVA-iodine reaction. Thus the presence of carbonyl groups in the main chain is not a main factor on the change of PVA-iodine reaction.

Consequently none of molecular weight, stereoregularity, the 1,2-glycol structure, and carbonyl group in the main chain may be a main factor govering the decrease of the color intensity of PVA-iodine reaction with the increase of fraction number. Other factors should be considered.

One of the possible structural variations which will affect the cystallinity and PVA-iodine reaction is branching of PVA, though the presence of branching on PVA has not been investigated in detail.

Imoto et al. reported that long branching, which was prepared by the chain transfer on the backbone of PVA, was scarecely found16). Murahashi et al. have found that long branching on PVA does not affect the PVA-iodine reaction17). This result is reasonable, for the presence of long branching probably show little effect with respect to the microstructure of PVA because of small number of branching point per a polymer molecule.

Short branching has not been confirmed and its presence has been only speculated. The presence of short branching, however, seems reasonable because of a similar reactivity of the vinyl acetate radical to that of ethylene and from the consideration of the chain transfer reaction of model compounds$^{18)}$. Short branching may be produced by the back biting mechanism. The high conversion will lead up to the low monomer concentration, and hence will produce different PVA molecules with respect to the frequency of short branching. In addition the gelation area of PVA surface film($\sim$10A^2/monomer unit) is equall to or less than the calculated two dimensional surface area of closed packing($\sim$12A^2/monomer unit), and the polymer molecules should be brought close to each other at gelation$^{19)}$. Therefore the presence of short branching probably disturbs both the PVA-iodine reaction and the formation of stable foam, the foam fractionation with respect to short branching being possible. At present, however, we must await the developement of a technique for the measurement of short branching.

In the case of Sample B prepared from the cationic polymerization, the color intensity of PVA-iodine reaction was weak owing to low syndiotacticity. It is noteworthy that color intensity of PVA contained in foam layers decrease with the increase of fraction number similar to the case of Sample A.

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