

# Ionic Graft Copolymerization. I.

## Homopolymerization of $\beta$ -Propiolactone by Sodium Acetate Catalyst

TETSUYA SHIOTA and YUTAKA GOTO, *Research Institute for Production Development, Kyoto, Japan*, and KOICHIRO HAYASHI, *Department of Polymer Chemistry, Kyoto University, Kyoto, Japan*

### Synopsis

The polymerization of  $\beta$ -propiolactone ( $\beta$ PL) by sodium acetate catalyst has been investigated. The polymerization behavior with monomer purified with calcium chloride was found to be a little different from that previously reported for this monomer. That is, poly- $\beta$ -propiolactone (P $\beta$ PL) obtained from  $\beta$ PL dried with  $\text{CaCl}_2$  has a higher degree of polymerization than that obtained from conventionally treated  $\beta$ PL, and its infrared spectrum shows type II configuration, which differs from that reported in previous papers. Some chain transfer reaction is observed even for the polymerization of the  $\text{CaCl}_2$ -dried  $\beta$ PL; however, this is less important in toluene. The electronegativity of the anion or cation in catalyst greatly influences the rate of polymerization.

### INTRODUCTION

$\beta$ -Propiolactone ( $\beta$ PL) has been easily polymerized thermally<sup>1,2</sup> by various kinds of catalysts<sup>1,3</sup> and by irradiation with ultraviolet<sup>4</sup> or  $\gamma$ -rays.<sup>5-7</sup> Purification of  $\beta$ PL was not so easy, because of the high polymerizability of  $\beta$ PL in the presence of desiccating agents.

$\beta$ PL could not be dried sufficiently by the usual desiccating agents such as  $\text{CaH}_2$ ,  $\text{Na}_2\text{SO}_4$ , Drierite,  $\text{BaO}$ , or  $\text{NaOH}$ , for a large amount of water (>300 ppm) remained in  $\beta$ PL after treatment with these desiccants. In the case of  $\beta$ PL dried with toluylene diisocyanate, the water content in  $\beta$ PL was estimated to be <10 ppm (Table I), but the degree of polymerization of P $\beta$ PL obtained was lower than that of polymer from monomer purified by  $\text{CaCl}_2$  (Table II). The authors found that when  $\beta$ PL was passed through calcium chloride quickly, it was desiccated sufficiently (>10 ppm of water content), as shown in Table I. This drying method may also remove some other impurities by partial polymerization of  $\beta$ PL. The polymerization behavior of  $\beta$ PL purified in this way was quite different from that of conventionally purified samples (Table II). The present study was carried out with the object of investigating the homopolymerization of purified  $\beta$ PL in comparison with the results of graft copolymerization.<sup>8</sup> In the case of the conventionally purified  $\beta$ PL, the molecular weight of P $\beta$ PL produced was very low and independent of the reaction time owing to chain

TABLE I  
Drying of  $\beta$ -Propiolactone

Expt. no.	Drying	Water content after drying, <sup>a</sup> ppm
1	CaH <sub>2</sub> (1 day)	570
2	CaH <sub>2</sub> (1 day), azeotropic distillation by benzene	350
3	CaH <sub>2</sub> (3 days)	300
4	Na <sub>2</sub> SO <sub>4</sub> (3 days)	1230
5	Na <sub>2</sub> SO <sub>4</sub> (3 days), Drierite (8 days)	330
6	Na <sub>2</sub> SO <sub>4</sub> (3 days), BaO (4 days)	330
7	Na <sub>2</sub> SO <sub>4</sub> (3 days), NaOH (90 min.)	340
8	Na <sub>2</sub> SO <sub>4</sub> (3 days), flow out over CaCl <sub>2</sub> quickly, two times	<10
9	Toluylene diisocyanate (2% for $\beta$ PL)	<10

<sup>a</sup> Water content before drying was 4150 ppm.

TABLE II  
Comparison of Monomer and Polymer with the Use of CaH<sub>2</sub>, CaCl<sub>2</sub>, and Toluylene Diisocyanate as Desiccating Agents for Monomer

	Monomer desiccation		
	CaH <sub>2</sub>	CaCl <sub>2</sub>	Toluylene diisocyanate
Monomer			
Water content, ppm	300-600	<10	<10
Boiling point, °C./mm.			
Hg	43/8	47/8	47/8
Polymer <sup>a</sup>			
Conversion, %	22	40	15
$[\eta]$ (CHCl <sub>3</sub> , 35°C.)	0.085	0.50	0.10
DP	32	350	39
Appearance	Powder	Fiber	Powder
Solubility	Partly soluble in hot CHCl <sub>3</sub>	Soluble in cold CHCl <sub>3</sub>	Soluble in cold CHCl <sub>3</sub>
Infrared spectrum	Type I	Type II	—

<sup>a</sup> Polymerization conditions: in bulk, CH<sub>3</sub>COONa, at 60°C. for 5 hr.

transfer; the infrared spectrum of polymer was of type I. For pure  $\beta$ PL, however, the molecular weight of P $\beta$ PL produced was considerably higher, and the infrared spectrum of the polymer was of type II.

## EXPERIMENTAL

### Reagents

$\beta$ PL obtained from Dainihon Celluloid Co. Japan was passed quickly through calcium chloride two times, followed by distillation at reduced pressure. The water content in the thus purified  $\beta$ PL was estimated to be

<10 ppm. by the Karl Fischer method (Table I). The degree of polymerization of P $\beta$ PL from purified  $\beta$ PL was higher, being about 10 times that obtained from conventionally purified  $\beta$ PL (Table II). Alkali metal acetates were dried at 98°C. for 3 hr. in high vacuum after predrying. Other catalysts, such as sodium isobutylate, sodium acrylate, and sodium hydroxide were also dried by the same method. Toluene, nitrobenzene, and dioxane were purified by the usual procedures.

### Polymerization Procedure

In the bulk polymerization, some amount (usually 3 cc.) of purified  $\beta$ PL was added to dried sodium acetate ( $3.1 \times 10^{-5}$  mole) in a dry box and the reaction tube was evacuated by using a high-vacuum technique (<10<sup>-4</sup> mm. Hg). In the solution polymerization, 1 cc. of  $\beta$ PL, 9 cc. of solvent, and  $3.1 \times 10^{-5}$  mole of catalyst were added into a reaction tube by the same procedure.

### Determination of Molecular Weight for Polymer

The molecular weight of P $\beta$ PL was determined by a viscometric method in chloroform at 35°C. by using the equation:<sup>9</sup>

$$[\eta] = 4.2 \times 10^{-4} M_n^{0.70} \quad (1)$$

### Determination of Endgroups of P $\beta$ PL<sup>10</sup>

**Determination in COOH Groups in P $\beta$ PL.** A 100-mg. portion of polymer was dissolved in 10 cc. of chloroform and titrated with 0.01*N* sodium methoxide-methanol standard solution with phenolphthalein as an indicator.

**Determination of Double Bonds in P $\beta$ PL.** A 100-mg. portion of polymer was dissolved in 10 cc. of acetic acid; 10 cc. of this polymer solution, 1 cc. of 0.01*N* bromine-acetic acid, and 1 cc. of 0.25% mercuric acetate solution were reacted in the dark for 30 min. in a sealed tube. After reaction 0.1 cc. of 10% KI aqueous solution was added and titration carried out with 0.01*N* Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub> solution.

### Determination of Water Content

The water content in  $\beta$ PL was determined by the Karl Fischer method, in which  $\beta$ PL did not affect the analysis.

## RESULTS

### Effect of Reaction Time on the Bulk Polymerization

$\beta$ PL was polymerized by sodium acetate. Figure 1 shows the time-conversion curve for the polymerization of  $\beta$ PL (H<sub>2</sub>O > 300 ppm) desiccated with calcium hydride, and Figures 2 and 3 show the polymerization at 60 and 30°C., respectively, of  $\beta$ PL (H<sub>2</sub>O < 10 ppm) desiccated by calcium

chloride. The degrees of polymerization of the polymers produced are quite different.

In the case of conventionally purified  $\beta$ PL, the degree of polymerization of polymer was estimated to be ca. 50 and was independent of the

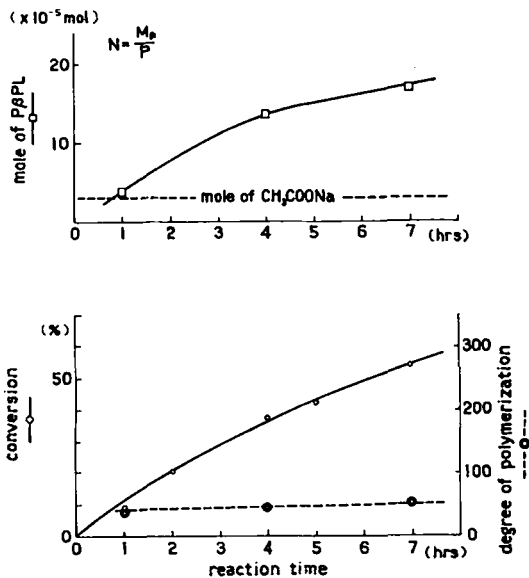


Fig. 1. Polymerization of  $\beta$ PL purified by  $\text{CaH}_2$ : ( $\square$ ) moles  $\text{P}\beta\text{PL}$ ; ( $\circ$ ) conversion; ( $\odot$ ) degree of polymerization.  $\beta\text{PL}$ , 1 cc.;  $\text{CH}_3\text{COONa}$ ,  $2.9 \times 10^{-5}$  mole ( $10^{-2}$  mole/l.);  $60^\circ\text{C}$ .; water content, 570 ppm;  $\text{H}_2\text{O}/\text{CH}_3\text{COONa} = 1.09$ .

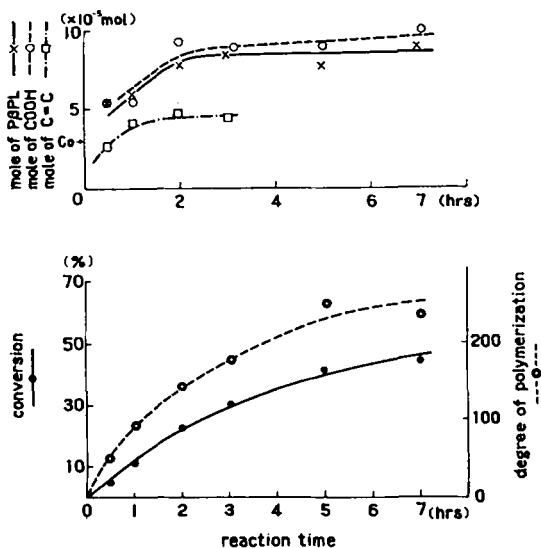


Fig. 2. Polymerization of  $\beta\text{PL}$  purified by  $\text{CaCl}_2$ : ( $\times$ ) moles  $\text{P}\beta\text{PL}$ ; ( $\circ$ ) moles  $\text{COOH}$ ; ( $\square$ ) moles  $\text{C}=\text{C}$ ; ( $\bullet$ ) conversion; ( $\odot$ ) degree of polymerization.  $\beta\text{PL}$ , 3 cc.;  $\text{CH}_3\text{COONa}$ ,  $3.1 \times 10^{-5}$  mole ( $10^{-2}$  mole/l.);  $60^\circ\text{C}$ .;  $\text{H}_2\text{O} < 10$  ppm.

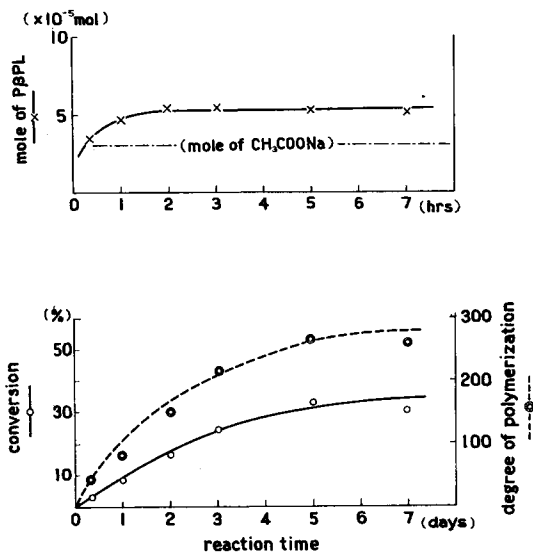


Fig. 3. Polymerization of  $\beta$ PL purified by  $\text{CaCl}_2$ : (X) moles of  $\text{P}\beta\text{PL}$ ; (O) conversion; (⊙) degree of polymerization.  $\beta\text{PL}$ , 3 cc.;  $\text{CH}_3\text{COONa}$ ,  $3.1 \times 10^{-5}$  mole ( $10^{-2}$  mole/l.);  $30^\circ\text{C}$ .;  $\text{H}_2\text{O} < 10$  ppm.

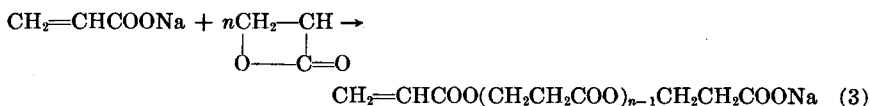
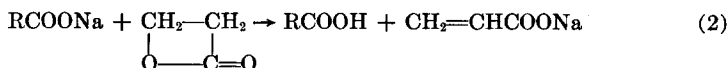
reaction time. Also, the number of moles of polymer formed increases with reaction time up to about 6 times the number of moles of catalyst for 7 hr. Apparently these results might be attributed to chain transfer caused by an impurity. The infrared spectrum of this  $\text{P}\beta\text{PL}$  shows a type I configuration. One of the authors has already reported similar results for the bulk polymerization of  $\beta\text{PL}$ .<sup>11</sup>

On the other hand, when  $\beta\text{PL}$  purified by calcium chloride was polymerized (Figs. 2 and 3), the degree of polymerization of  $\text{P}\beta\text{PL}$  increased with reaction time up to about 250, which is about 5 times that of the polymer of conventionally purified  $\beta\text{PL}$ , and the number of moles of polymer produced in the reaction system was only 1-3 times the number of moles of catalyst present. Chain transfer is reduced and occurs predominantly in the earlier period of polymerization. It may be concluded that for sufficiently purified monomer, the degree of polymerization of polymer formed is comparatively higher, even in bulk, and the polymer configuration is of type II as revealed by the infrared spectrum. In spite of a reversible conversion of the configuration, it is interesting that the type II infrared spectrum of  $\text{P}\beta\text{PL}$  is obtained with sodium acetate, because previous papers<sup>11,12</sup> reported that a type I configuration was obtained with alkali catalysts. The number of polymer molecules increases with reaction time in the earlier period but thereafter remains almost constant.

The increase in the number of polymer molecules in the earlier period may be attributed to the increase of initiating efficiency and solubility of catalyst, and after this period the chain transfer reaction hardly occurs. Also, in the graft copolymerization of  $\beta\text{PL}$  onto acrylonitrile-sodium acry-

late copolymer,<sup>8</sup> the grafting efficiency is observed to be about 60%, independent of the reaction time, and this result shows that the chain transfer reaction occurs frequently in the earlier period of polymerization but rarely in the later stages. The double bond content in the polymer was estimated to be about 0.5 groups per polymer molecule.

It would appear that about 50% of the polymer molecules was produced by the chain transfer reaction, because polymer having a double bond in the polymer chain end would be produced by a chain transfer reaction as shown in eqs. (2) and (3).



This result coincides with the fact that the efficiency of grafting  $\beta$ PL on acrylonitrile-sodium acrylate copolymer is limited to 60%.

### Effect of Reaction Temperature

The bulk polymerization of  $\beta$ PL induced by sodium acetate at various temperatures is shown in Figure 4. The activation energy calculated from the Arrhenius plot in Figure 5 is 23 kcal./mole. For the graft copolymerization onto acrylonitrile-sodium acrylate copolymer, the activation energy is 24.6 kcal./mole, which coincides closely with the previous result. These values are higher than the energies reported by other workers, which are 11 kcal./mole for the pyridine-catalyzed polymerization,<sup>13</sup> 16 kcal./mole for the alkali-catalyzed polymerization, and 19 kcal./mole for the photoinduced polymerization in the presence of uranyl nitrate.<sup>4</sup> Such higher activation energies may be attributed to differences in nature of catalyst or purity of the monomer.

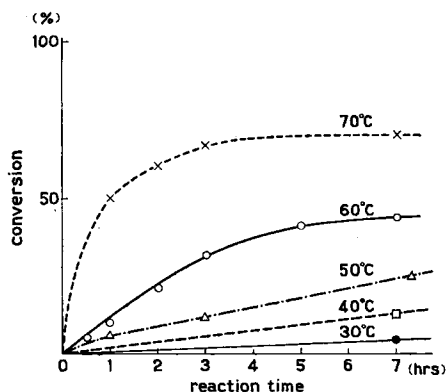


Fig. 4. Effect of temperature on the polymerization of  $\beta$ PL.  $\beta$ PL, 3 cc.;  $\text{CH}_3\text{COONa}$ ,  $3.1 \times 10^{-5}$  mole ( $10^{-2}$  mole/l.);  $\text{H}_2\text{O} < 10$  ppm.

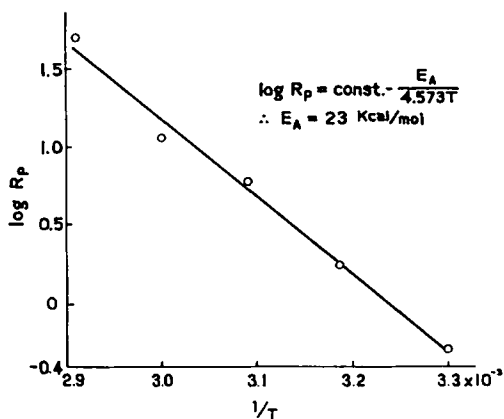


Fig. 5. Arrhenius plot for the  $\text{CH}_3\text{COONa}$ -catalyzed polymerization of  $\beta\text{PL}$  in bulk.

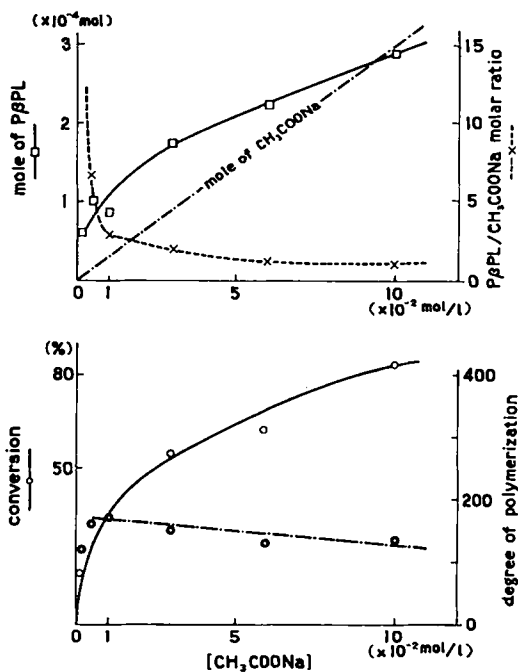


Fig. 6. Effect of  $\text{CH}_3\text{COONa}$  concentration on polymerization of  $\beta\text{PL}$ ; ( $\square$ ) moles  $\text{P}\beta\text{PL}$ ; ( $\times$ ) molar ratio of  $\text{P}\beta\text{PL}/\text{CH}_3\text{COONa}$ ; ( $\circ$ ) conversion; ( $\odot$ ) degree of polymerization.  $\beta\text{PL}$ , 3 cc.;  $60^\circ\text{C}$ .; 3 hr.;  $\text{H}_2\text{O} < 10 \text{ ppm}$ .

### Effect of Catalyst Concentration

The effect of catalyst concentration on the bulk polymerization of  $\beta\text{PL}$  at a fixed reaction time is shown in Figure 6; the degree of polymerization decreases with catalyst concentration. The number of polymer molecules decreases with decreasing catalyst concentration but does not coincide

completely with the number of molecules of catalyst added. One reason is the instability of the polymer at higher degrees of polymerization. The ratio of number of molecules of P $\beta$ PL per molecule catalyst is higher at lower concentrations of catalyst and is close to unity at the higher concentrations. A ratio higher than unity may be caused by chain transfer to monomer or traces of impurity, but not by depolymerization, thermal polymerization, or polymerization by impurity, as  $\beta$ PL did not polymerize without catalyst at this temperature and scission of polymer could hardly proceed in the presence of this catalyst. In the catalyst concentration range of  $6 \times 10^{-2}$  to  $1 \times 10^{-2}$  mole/l., the ratio of polymer and catalyst is approximately unity. However, the dependence on catalyst concentration might be attributed to the initiation efficiency, association, and solubility of catalyst.

### Solution Polymerization of $\beta$ PL

$\beta$ PL was polymerized by the same catalyst in solvents of different dielectric constants, i.e., toluene, dioxane, and nitrobenzene (Fig. 7 and

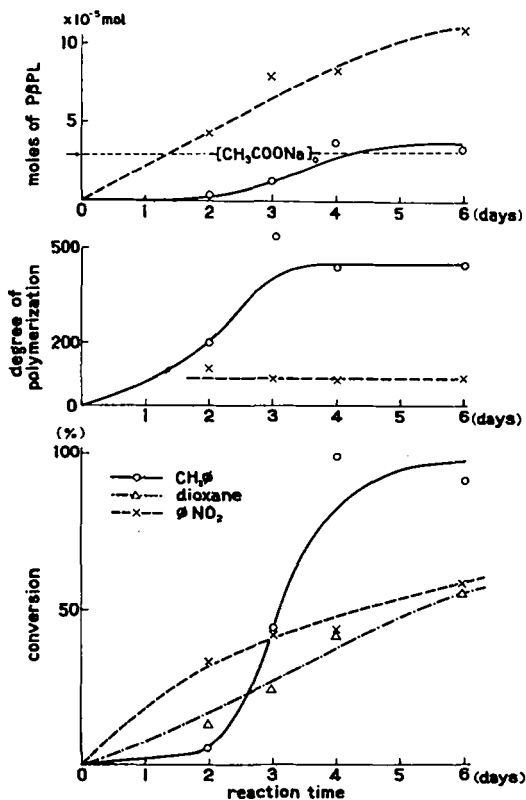


Fig. 7. Solution polymerization of  $\beta$ PL; moles of P $\beta$ PL, degree of polymerization, and conversion in (O) toluene, ( $\Delta$ ) dioxane, and (X) nitrobenzene.  $\beta$ PL, 1 cc.; solvent, 9 cc.;  $\text{CH}_3\text{COONa}$ ,  $3.1 \times 10^{-4}$  mole ( $3.1 \times 10^{-3}$  mole/l.);  $60^\circ\text{C}$ .



Table III). The catalyst is insoluble in these solvents, and P $\beta$ PL is insoluble in toluene, partially soluble in dioxane, and soluble in nitrobenzene. The polymerization in toluene proceeds heterogeneously for the whole process and shows an induction period in which polymerization proceeds very slowly and conversion is limited to only 5% for 2 days. At the end of the induction period, the number of polymer molecules is only about 1/8 of the catalyst number, but the degree of polymerization is already comparatively high, about 200. After the induction period, polymerization proceeds rapidly, and the number of polymer molecules and the degree of polymerization increase together. In this period, the increase in the degree of polymerization is limited to about 2 times, but the increase of the number of polymer molecules is about 10 times, and so the conversion increases about 20 times. It would appear that the accelerating effect is caused by an increase of active points.

TABLE III  
Solution Polymerization of  $\beta$ PL

	Bulk polymerization	Solution polymerization		
		Nitrobenzene	Dioxane	Toluene
Reaction time, days	7 hr.	6	6	6
Conversion, %	44	58	55	91
Degree of polymerization	240	85	—	440
Molar ratio of				
P $\beta$ PL/CH <sub>3</sub> COONa	3.0	3.5	—	1.1
Dielectric constant of solvent	~42	34.3	2.23	~2.38
Solubility of P $\beta$ PL	1	2	3	4

As described above, the number of polymer molecules increases very little in the induction period, but increases rapidly after that, and at last reaches the same number as that of catalyst. Since toluene does not dissolve either catalyst or P $\beta$ PL, it may be supposed that  $\beta$ PL is polymerized only at the surface of catalyst in the initial stage; after that polymer is stripped off from the catalyst surface and fresh catalyst surface initiates successive polymerizations. In the graft copolymerization of  $\beta$ PL onto acrylonitrile-sodium acrylate copolymer, no induction period is observed in toluene, because active points do not associate and all active points initiate the graft copolymerization simultaneously.

The higher degree of polymerization for the polymerization in toluene and higher grafting efficiency (about 90%) for the graft copolymerization in toluene<sup>8</sup> may demonstrate that chain transfer does not occur in toluene to an appreciable extent. In the earlier stage of polymerization, the order of rate of polymerization for the nature of solvent is nitrobenzene > dioxane > toluene, which depends on the dielectric constant. After the induction period, the order of rate of solution polymerization is toluene > nitrobenzene > dioxane which is the same order as for graft copolymerization.<sup>8</sup> One reason for the accelerating effect for the polymerization in toluene is the

precipitation of propagating active species. Kagiya et al.<sup>15</sup> have reported also that the rate of solution polymerization of  $\beta$ PL by pyridine catalyst was less in toluene than in nitrobenzene.

### Effect of Presence of Air

The presence of air has no remarkable effect on the polymerization behavior of  $\beta$ PL, as shown in Table IV.

TABLE IV  
Effect of Presence of Air on the Polymerization of  $\beta$ PL\*

Expt. no.	Atmosphere	Reaction time, hr.	Conversion, %	Degree of polymerization
1	Air	0.5	6	53
2		2.0	24	130
3	Vacuum	0.5	5	46
4	(degassed once)	2.0	21	145
5	Vacuum	0.5	5	50
6	(degassed 3 times)	2.0	22	137

\*  $\beta$ PL, 3 cc.;  $\text{CH}_3\text{COONa}$ ,  $3 \times 10^{-5}$  mole;  $60^\circ\text{C}$ .

### Effect of the Cation of Alkali Metal Acetate Catalyst

$\beta$ PL was polymerized by various alkali metal acetates, i.e.,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{H}^+$ ,  $\text{Ba}^{++}$ ,  $\text{Ca}^{++}$  acetates. The rate of polymerization increases in the order:  $\text{K}^+ > \text{Na}^+ > \text{Li}^+ > \text{H}^+$ ;  $\text{Ba}^{++} > \text{Ca}^{++}$ , which is the reverse of the order of electronegativity of cations (Table V).

Lower electronegativity of a countercation may contribute to the dissociation of the ion pair, and therefore, the rate of polymerization is in-

TABLE V  
Effect of Cation in Catalyst on the Polymerization of  $\beta$ PL\*

Expt. no.	Catalyst		Electro-negativity of cation	Reaction time, hr.	Conversion, %
	Anion	Cation			
1	$\text{CH}_3\text{COO}^-$	$\text{K}^+$	0.8	0.5	54.7
2	"	"	"	7	~100
3	"	$\text{Na}^+$	0.9	0.5	5.3
4	"	"	"	7	43.9
5	"	$\text{Li}^+$	1.0	7	11.1
6	"	$\text{H}^+$	2.1	7	0.14
7	"	"	"	24	3.5
8	"	$\text{Ba}^{++}$	0.9	7	1.42
9	"	"	"	24	29.3
10	"	$\text{Ca}^{++}$	1.0	7	0.8
11	"	"	"	24	9.4

\*  $\beta$ PL, 3 cc.; catalyst,  $3.0 \times 10^{-5}$  mole;  $60^\circ\text{C}$ .

TABLE VI  
Effect of Anion of Catalyst on the Polymerization of  $\beta$ PL<sup>a</sup>

Expt. no.	Catalyst		pK <sub>a</sub>	Rate of polymerization, %/hr.	$\overline{DP}$	Molar ratio of P $\beta$ PL/catalyst	Molar ratio of C=C/P- $\beta$ PL
	Cation	Anion					
1	Na <sup>+</sup>	OH <sup>-</sup>	14.0	38	165	2.6	0.6
2	"	(CH <sub>3</sub> ) <sub>2</sub> CHCOO <sup>-</sup>	4.84	28	133	2.5	0.6
3	"	CH <sub>3</sub> COO <sup>-</sup>	4.76	26	153	2.0	0.4
4	"	CH <sub>2</sub> =CHCOO <sup>-</sup>	4.25	12	109	1.3	0.8

<sup>a</sup>  $\beta$ PL, 9 cc.; catalyst,  $9.3 \times 10^{-3}$  mole; 60°C.

creased. Higashimura et al.<sup>11</sup> have reported that the rate of polymerization of  $\beta$ PL by alkali metal hydroxides and carbonates as catalyst follows the order:  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+$ , which coincides with our result.

### Effect of Anion on Catalyst

$\beta$ PL was polymerized by alkali catalysts with various anions, i.e., sodium hydroxide, sodium isobutylate, sodium acetate, and sodium acrylate (Table VI). Polymerization activity is defined by the acidity of the anion. The rate of polymerization increases in the order:  $\text{NaOH} > (\text{CH}_3)_2\text{CHCOONa} > \text{CH}_3\text{COONa} > \text{CH}_2=\text{CHCOONa}$ , which is the same order as acidity of anions. The anion of higher acidity, that is, the anion of higher electron density, may attack the  $\beta$ -carbon of  $\beta$ PL more easily in the initiation step. This suggests chain transfer so that the ratio of number of molecules of polymer to catalyst molecules is higher than unit. A chain transfer reaction is apt to occur more frequently with catalyst of higher polymerization activity, in the order:  $\text{NaOH} > (\text{CH}_3)_2\text{CHCOONa} > \text{CH}_3\text{COONa} > \text{CH}_2=\text{CHCOONa}$ .

### Dilatometric Study of Polymerization of $\beta$ PL by $\text{CH}_3\text{COONa}$ Catalyst

In the batch system, the lower molecular weight polymers might be partly soluble in methanol. Therefore, it is desirable to determine conversions by means of gas chromatography or dilatometry. In the case of the gas chromatographic method, a correct determination could not be

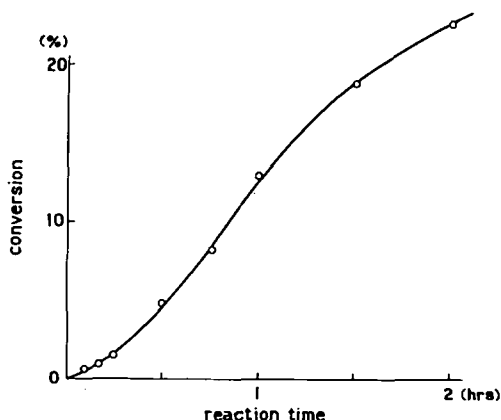


Fig. 8.  $\text{CH}_3\text{COONa}$ -catalyzed polymerization of  $\beta$ PL by dilatometry.  $\beta$ PL, 3 cc.;  $\text{CH}_3\text{COONa}$ ,  $3.1 \times 10^{-6}$  mole;  $60^\circ\text{C}$ .

expected for the reason of polymerization during measurements. Therefore,  $\beta$ PL was polymerized in bulk (Fig. 8), and in toluene and in nitrobenzene (Fig. 9) by using the dilatometric method.

These results coincide closely with those obtained in the batch system.

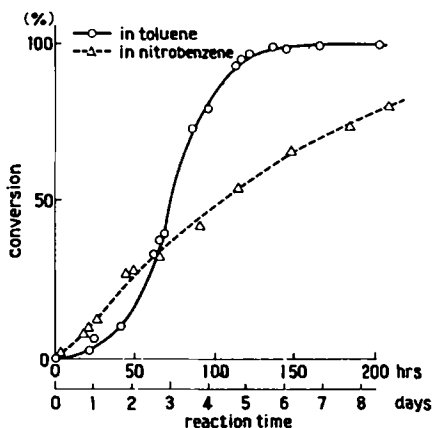


Fig. 9. Solution polymerization of  $\beta$ PL by dilatometry. (O) in toluene; ( $\Delta$ ) in nitrobenzene.  $\beta$ PL, 0.5 cc.; solvent, 4.5 cc.;  $\text{CH}_3\text{COONa}$ ,  $1.55 \times 10^{-4}$  mole;  $60^\circ\text{C}$ .; *in vacuo*.

### Depolymerization of P $\beta$ PL in $\gamma$ -Butyrolactone

One of the possible reasons for the fact that more than one chain of polymer is obtained from one catalyst molecule in the bulk polymerization is the degradation of P $\beta$ PL formed. Degradation of P $\beta$ PL was investigated in  $\gamma$ -butyrolactone under the same conditions as the bulk polymerization (Fig. 10). The nonpolymerizability of  $\gamma$ -butyrolactone is demonstrated by the fact that above 100% of polymer is never withdrawn. The intrinsic viscosity of reprecipitated polymer hardly changed with reaction time. The average number of scissions per polymer molecule was calculated, by means of the equation presented by Sakurada et al.,<sup>14</sup> to be 0.05–0.34. Therefore, the increase in the number of polymer molecules must be below

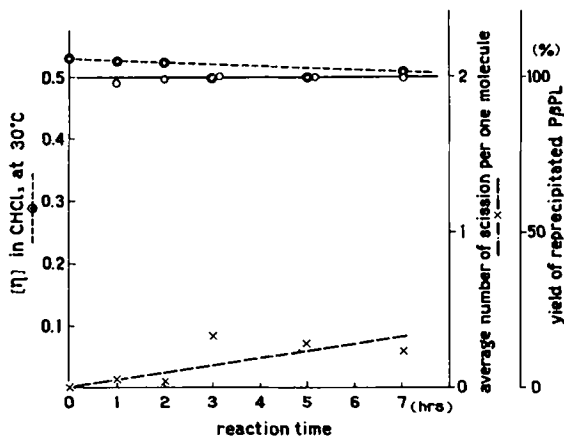


Fig. 10. Degradation of P $\beta$ PL in  $\gamma$ -butyrolactone: (●)  $[\eta]$  in  $\text{CHCl}_3$  at  $30^\circ\text{C}$ .; (X) average number of scissions per molecule; (O) yield of reprecipitated P $\beta$ PL. P $\beta$ PL 400 mg.;  $\text{CH}_3\text{COONa}$ ,  $3.1 \times 10^{-6}$  mole  $\gamma$ -butyrolactone, 2.6 cc.;  $60^\circ\text{C}$ .; *in vacuo*.

TABLE VII  
Determination of Acid Groups in P $\beta$ PL

Expt. no.	Reaction time, hr.	Conversion, %	[ $\eta$ ]	Measurement of degree of polymerization				Determination of COOH		C=C $\times 10^{-6}$ , mole
				$\overline{DP}$	P $\beta$ PL, $\times 10^{-6}$ , mole	Mole ratio P $\beta$ PL/ CH <sub>3</sub> COON <sup>a</sup>	$\times 10^{-6}$ , mole	$\overline{DP}^a$		
1	0.5	5.3	0.127	50	5.1	1.64	5.3	48	2.6	
2	1	10.7	0.182	92	5.6	1.81	5.3	97	4.0	
3	2	22.0	0.250	137	7.8	2.51	9.1	117	4.5	
4	3	31.5	0.300	179	8.5	2.74	8.9	171	4.4	
5	5	40.4	0.391	252	7.7	2.48	9.0	214	—	
6	7	43.9	0.370	236	8.9	2.87	10.0	212	—	

<sup>a</sup> Degree of polymerization calculated from amount of —COOH assuming that all polymers have carboxy endgroup.

1.3 times. This result does not coincide with the production of about 2 times the number of polymer molecules per catalyst molecule in the bulk polymerization. The increase in number of polymer molecules formed during the bulk polymerization should not then be mainly attributed to simultaneous depolymerization.

### Determination of Endgroups of P $\beta$ PL

The number of polymer molecules, calculated as a ratio of polymerization yield and molecular weight of polymer, was compared with the number of carboxyl groups and double bonds at the end of the polymer chain. The number of carboxyl groups is almost equal to the number of polymer molecules (Table VII). One end of the polymer chain will be composed of a carboxyl group as reported by Yamashita et al.<sup>10</sup> and David et al.<sup>6,7</sup> The other end of the polymer chain is supposed to be an acetyl group from the catalyst and double bond by chain transfer. Results for analysis for the double bond showed some scatter, but the number of double bonds tended to increase with reaction time. The number of polymer molecules, carboxyl groups, and double bonds initially increases with reaction time, and all then tend to a limiting value. These results suggest chain transfer by monomer or traces of impurity.

### Structure of Polymer

In previous papers,<sup>11,12</sup> it has been reported that the infrared spectrum of P $\beta$ PL polymerized by alkali catalyst is of type I and that of P $\beta$ PL obtained with acid catalyst is of type II. It was found that polymers from  $\beta$ PPL purified by different methods showed a different type of infrared spectrum. When  $\beta$ PPL is purified with the usual desiccating agents, Na<sub>2</sub>SO<sub>4</sub> or CaH<sub>2</sub>, the infrared spectra of P $\beta$ PL obtained by alkali or acid catalyst are of type I and type II, respectively. When  $\beta$ PPL is purified by CaCl<sub>2</sub>, the polymers obtained with alkali or acid catalyst, both show type II infrared spectra.

In the case of  $\beta$ PPL purified by CaCl<sub>2</sub>, the P $\beta$ PL obtained was about 10 times higher in molecular weight than polymer from the conventionally purified  $\beta$ PPL; it was fibriform in appearance and was easily soluble in cold CHCl<sub>3</sub>. On the other hand, polymer from conventionally purified monomer was powdery and only partially soluble in cold CHCl<sub>3</sub>, as shown in Table II and Figures 1 and 2. Yamashita et al.<sup>15</sup> have reported that infrared spectra of P $\beta$ PL polymerized by AlEt<sub>3</sub>-H<sub>2</sub>O catalyst are of type I for polymer of low molecular weight and of type II for polymer of high molecular weight. The dependency between infrared spectra and degree of polymerization of P $\beta$ PL obtained from  $\beta$ PPL purified by CaCl<sub>2</sub> was investigated (Table VIII). It was concluded that polymer obtained by alkali catalyst from pure  $\beta$ PPL shows a type I spectrum for low molecular weight material and a type II spectrum for high molecular weight polymer.

TABLE VIII  
Infrared Spectrum of P $\beta$ PL

Reaction time, hr.	Polymerization of $\beta$ PL purified with $\text{CaCl}_2$				Polymerization of $\beta$ PL purified with $\text{CaH}_2$					
	$\text{CH}_3\text{COONa}$		$\text{CH}_2=\text{CHCOONa}$		$\text{NaOH}$		$\text{CH}_3\text{COONa}$		$\text{NaOH}$	
	Spectrum type	$[\eta]$	Spectrum type	$[\eta]$	Spectrum type	$[\eta]$	Spectrum type	$[\eta]$	Spectrum type	$[\eta]$
0.5	I	0.13	I < II	0.16	II	0.24	—	—	—	—
1	I > II	0.18	II	0.26	II	0.33	I	0.07	—	—
2	II	0.25	—	—	—	—	—	—	—	—
3	II	0.30	—	—	—	—	—	—	—	—
7	II	0.37	—	—	—	—	I	0.11	I	0.10



## DISCUSSION

The rate of polymerization is given by eq. (4):

$$-d[M]/dt = k_p[C^*][M] = \alpha k_p[Co][M] \quad (4)$$

where  $[C^*]$  denotes concentration of growing active center,  $[Co]$  is initial catalyst concentration,  $[M]$  is monomer concentration,  $\alpha$  is the efficiency of initiation of catalyst, and the other symbols have their usual meaning. It was found that  $\alpha$  is almost unity but varies with the nature of catalyst, solvent, temperature, and polymerization time because of solubility, association, and efficiency of initiation. The reaction of  $\beta$ PPL with sodium acetate has been investigated by Gresham et al.<sup>3</sup> and Higashimura et al.<sup>11</sup> Gresham et al. pointed out that the ring opening of  $\beta$ PPL in the alkali-catalyzed reactions occurs at the oxygen-methylene bond. Their argument was supported by the result that one end of the polymer was a carboxyl group. In the bulk polymerization of  $\beta$ PPL by alkali catalysts, polymer having a higher degree of polymerization could not be obtained before the present work. This is attributed to chain transfer to impurities in the monomer, because polymer of comparatively higher molecular weight may be obtained from exceptionally carefully purified monomer. However, even in the case of  $\beta$ PPL purified by  $CaCl_2$ , chain transfer reaction cannot be completely eliminated. Depolymerization hardly occurs under these reaction conditions. Polymerization of  $\beta$ PPL catalyzed by "living"  $\alpha$ -methylstyrene tetramer was attempted with the careful operations by Sumitomo et al.,<sup>16</sup> but they also observed chain transfer to monomer.

For the polymerization in toluene, in which the catalyst is very insoluble, a considerably longer induction period is observed; after that, polymerization proceeds very rapidly. In the induction period, the number of polymer molecules increases very slowly, but the polymer obtained has already a considerably higher degree of polymerization. These results demonstrate that only part of the catalyst initiates the polymerization on the surface. During this period, polymer produced on the surface of catalyst strips off and fresh catalyst may initiate successive polymerizations. A higher degree of polymerization in toluene demonstrates that chain transfer hardly occurs in toluene. Higashimura et al.<sup>11</sup> have also reported results similar to ours. On comparing the polymerizations in toluene, dioxane, and nitrobenzene, the order of rate of polymerization in the initial period is: nitrobenzene > dioxane > toluene, which corresponds to the order of dielectric constant.

However, after this period, the rate of polymerization in toluene is higher than in the other two solvents. One of the reasons may be that the propagating active species precipitates and polymerization proceeds inhomogeneously. In the polymerization of  $\beta$ PPL by alkali metal acetates, the nature of the counteranion influences the rate of propagation. The rate of polymerization increases in the reverse order to the electronegativity of cation. Salts of metals having lower electronegativity will dissociate to ions easily, and therefore monomer may easily approach the active species.

In the polymerization of  $\beta$ PL by organic salts, the anion of the catalyst is also effective for the polymerization activity; that is, the higher acidity of the anion favors higher polymerization activity. In the polymerization of  $\beta$ PL induced by alkali catalyst, the growing active species is primary carboxylate;<sup>1,3,11</sup> therefore, the anion of the catalyst will not influence the rate of propagation but will influence the rate of initiation. However, in a heterogeneous polymerization system in which the catalyst is almost insoluble and the ions are associated with each other, the anion of the catalyst may influence the propagation step by influencing formation of a complicated counteraction associated with catalyst molecule.<sup>11</sup>

The order of the rate of polymerization for catalysts having various anions corresponds to the order of acidity of the anion (Table VI), and also coincides with the order of magnitude of the degree of polymerization and the mole ratio of  $P\beta$ PL and catalyst molecule. It seems that the  $pK_a$  of the anion of the catalyst influences the initiating efficiency or solubility of catalyst and the rate of propagation.

### CONCLUSION

It was found that the polymerization behavior of sufficiently purified  $\beta$ PL was a little different from that reported by other workers. The polymer of  $\beta$ PL dried with  $\text{CaCl}_2$  has a higher molecular weight than that of conventionally purified  $\beta$ PL, and has a type II infrared spectrum. Some chain transfer is observed even for the polymerization of such purified  $\beta$ PL, but very little chain transfer occurs in toluene. Polymerization activity is affected by the nature of anion and counteraction of catalyst; the lower electronegativity of anion or counteraction favor higher polymerization activity.

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### Résumé

La polymérisation de la  $\beta$ -propiolactone ( $\beta$ PL) au moyen d'un catalyseur acétate de sodium a été étudiée. Le comportement à la polymérisation a utilisant du monomère purifié sur du chlorure de calcium a été trouvé être légèrement différent des rapports précédents. Ceci signifie que la poly- $\beta$ -propiolactone (P- $\beta$ PL) obtenue au départ de  $\beta$ PL purifiée sur  $\text{CaCl}_2$  à un degré de polymérisation plus élevé que celle obtenue au départ de  $\beta$ PL obtenue de façon habituelle et son spectre infrarouge montre que la configuration de type II diffère de celle rapportée dans le manuscrit précédent. Une certaine réaction de transfert de chaîne est observée même pour la polymérisation d'une telles  $\beta$ PL purifiée; toutefois, elle est moins importante dans le toluène. L'électronégativité des anions en croissance ou du cation de signe contraire influence fortement la vitesse de Polymérisation.

### Zusammenfassung

Die Polymerisation von  $\beta$ -Propiolacton ( $\beta$ PL) mit Natriumacetat als Katalysator wurde untersucht. Das Polymerisationsverhalten des mit Kalziumchlorid gereinigten Monomeren unterschied sich etwas von dem in früheren Berichten angegebenen. Poly- $\beta$ -propiolacton (P- $\beta$ PL) aus dem mit  $\text{CaCl}_2$  gereinigtem  $\beta$ PL hat nämlich einen höheren Polymerisationsgrad als das aus dem in üblicher Weise gereinigten  $\beta$ PL erhaltene und sein Infrarotspektrum zeigt die, von den der in früheren Mitteilungen beschriebenen verschiedene Typ-II-Konfiguration. Auch bei der Polymerisation des derartig gereinigten  $\beta$ PL wird eine gewisse Kettenübertragung beobachtet; sie hat in Toluol weniger Bedeutung. Die Elektronegativität des wachsenden Anions oder des Gegenkations besitzt grossen Einfluss auf die Polymerisationsgeschwindigkeit.

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