

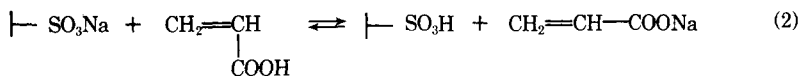
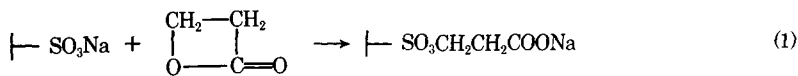
## Ionic Graft Copolymerization.

### V. Graft Copolymerization of $\beta$ -Propiolactone onto the Trunk Polymers Containing Carboxylic Acid, Sulfonic Acid, and Other Salts

TETSUYA SHIOTA and YUTAKA GOTO, *Ōmikenshi Spinning Co., Ltd., Awazi-cho, Higashi-ku, Osaka, Japan*, and KOICHIRO HAYASHI and SEIZO OKAMURA, *Department of Polymer Chemistry, Kyoto University, Kyoto, Japan*

#### Synopsis

$\beta$ -Propiolactone ( $\beta$ PL) was graft-copolymerized onto styrene-divinylbenzene copolymers containing various carboxylates or sulfonates, composed of anions and cations having different electronegativities. In parallel, the mechanism of polymerizations of  $\beta$ PL by relatively neutral catalysts was studied in comparison with the behaviors of graft copolymerizations. In the graft copolymerization onto the trunk polymer containing various carboxylates, a lower electronegativity of counteraction favors a higher anionic polymerization activity and the order of rate of polymerization coincides with that of anionic activities of catalysts. On the other hand, in the case of trunk polymer containing sulfonates, a higher electronegativity of counteraction favors a cationic polymerization activity, and the order of rate of polymerization coincides with that of cationic activity of catalyst. The order of grafting efficiency at fixed total conversion coincides almost with that of anionic activity. The comparatively higher grafting efficiency in the grafting onto trunk polymer containing carboxylic acid might support an anionic graft copolymerization mechanism by carboxyl anion. The two following mechanisms were proposed for the initiation of the polymerization by the trunk polymer containing sodium sulfonate, in which acrylic acid is transformed from  $\beta$ PL.

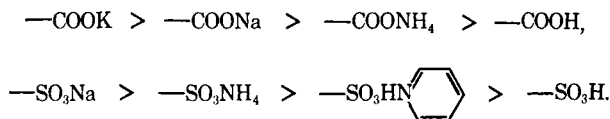


#### INTRODUCTION

In our previous paper,<sup>1</sup> the polymerization mechanisms of  $\beta$ PL by a relatively neutral catalyst such as sodium toluene sulfonate and acetic acid have been studied in comparison with the behavior of polymerizations by cationic catalyst ( $\text{CH}_3\text{OSO}_3\text{H}$ ) and anionic catalyst ( $\text{CH}_3\text{COONa}$ ).

In this paper, the behaviors of the graft copolymerizations of  $\beta$ PL onto various trunk polymers containing carboxylic acid, sulfonic acid, and their

salts were compared. The natures of the catalysts used are summarized in Table I. The basicities of these catalysts decrease in the order:







The anionic polymerization activities of these catalysts are in the order of their basicities, and the cationic polymerization activities are in the inverse order. In Table I, the catalyst in the upper left-hand corner is a typical anionic catalyst, that in the lower right-hand corner is a cationic one, that in the upper right-hand corner is a covalent neutral one, and that in the lower left-hand corner is an ionic neutral one.

Since anions in these catalysts combine with trunk polymers by a covalent bond, the grafting efficiency (percentage of grafted polymer to total polymer polymerized) is expected to be higher in anionic polymerization and to be lower in cationic polymerization. Chain-transfer reactions to monomer, impurity, or trunk polymer also have an influence on the grafting efficiency. It was found in our previous paper<sup>2</sup> that chain transfer to monomer occurs only to a very small extent in anionic polymerization in toluene. Therefore,  $\beta$ PL was graft-copolymerized in toluene solution in this work.

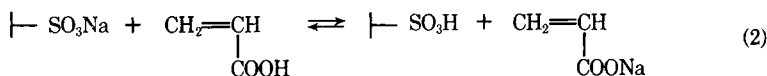
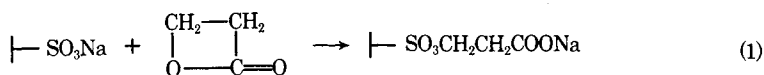
Styrene (St)-divinylbenzene (DVB)-acrylic acid (AA) copolymer, sulfonated St-DVB copolymer and their alkaline salts were used as trunk polymer for the following reasons: (1) St-DVB copolymer is sulfonated easily; (2) the graft copolymer is separated easily by solvent extraction, because these trunk polymers are crosslinked and insoluble.

TABLE I  
Nature of Catalysts

		←More electrophilic→				Weak acid or weak base (covalent, non-dissociable)	
Strong base (anionic initiator)		Cations					
Anions	K <sup>+</sup> (0.8) <sup>a</sup>	Na <sup>+</sup> (0.9) <sup>a</sup>	NH <sub>4</sub> <sup>+</sup>		H <sup>+</sup> (2.1) <sup>a</sup>		
OH <sup>-</sup>	KOH	NaOH	NH <sub>4</sub> OH (4.75) <sup>b</sup>	 (880) <sup>b</sup>	HOH (14.0) <sup>b</sup>		
CH <sub>3</sub> COO <sup>-</sup>	CH <sub>3</sub> COOK	CH <sub>3</sub> COONa	CH <sub>3</sub> COONH <sub>4</sub>	CH <sub>3</sub> COOHN 	CH <sub>3</sub> COOH (4.76) <sup>c</sup>		
CH <sub>3</sub> φSO <sub>3</sub> <sup>-</sup>	CH <sub>3</sub> φSO <sub>3</sub> K	CH <sub>3</sub> φSO <sub>3</sub> Na	CH <sub>3</sub> φSO <sub>3</sub> NH <sub>4</sub>	CH <sub>3</sub> φSO <sub>3</sub> HN 	CH <sub>3</sub> φSO <sub>3</sub> H (0.40) <sup>c</sup>		
Neutral salt (ionic, dissociable)						Strong acid (cationic initiator)	

<sup>a</sup> Electronegativity, <sup>b</sup> pK<sub>b</sub>, <sup>c</sup> pK<sub>a</sub>.

In the graft copolymerization onto trunk polymer containing various carboxylates, lower electronegativity of the counteranion favors a higher anionic polymerization activity, and the order of rate of polymerization coincides with that of the anionic activity of catalyst. On the other hand, in the case of trunk polymers containing sulfonates, a higher electronegativity of the counteranion favors higher cationic polymerization activity, and the order of rate of polymerization coincides with that of the cationic activity of catalyst. The order of grafting efficiency at a fixed total conversion is almost coincident with that of the anionic activity. The comparatively higher grafting efficiency in grafting onto the trunk polymer containing carboxylic acid supports an anionic graft-copolymerization mechanism by carboxyl anion. The two following mechanisms are proposed for the initiation of the polymerization by the trunk polymer containing sodium sulfonate, where acrylic acid is transformed from  $\beta$ P.L.



## EXPERIMENTAL

### Reagents

$\beta$ P.L. was purified by the same methods as described in our previous paper.<sup>3</sup> Styrene (St), divinylbenzene (DVB), acrylic acid (AA), benzene, and toluene were purified by the usual procedures.

### Preparation of St-DVB Copolymer

St-DVB copolymer was prepared by copolymerization of St (0.226 mole) and DVB (0.0451 mole) by benzoyl peroxide (150 mg) in benzene (33 cc) *in vacuo* at 60°C for 15 hr. A 100–200 mesh powder of polymer was used as trunk polymer.

### Preparation of Trunk Polymer Containing —COOH

The trunk polymer containing —COOH was prepared by copolymerization of St (0.226 mole), DVB (0.0451 mole), and AA (0.188 mole) by benzoyl peroxide (150 mg) in benzene (33 cc) solution *in vacuo* at 60°C for 72 hr. A 100–200 mesh powder of polymer was used as trunk polymer. This trunk polymer had a carboxylic acid group content of  $4.54 \times 10^{-4}$  mole 0.1 g of trunk polymer.

### Preparation of the Trunk Polymer Containing —SO<sub>3</sub>H

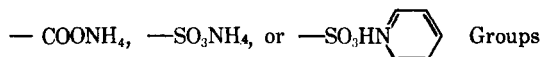
Powder of St-DVB copolymer (10 g) was reacted with chlorosulfonic acid (48 cc) in chloroform (300 cc) at 15°C for 15 hr, the product was poured

into glacial acetic acid (170 cc) and then was washed with distilled water. A 100–200 mesh powder of polymer was used as trunk polymer. This trunk polymer has a sulfonic acid group content of  $4.38 \times 10^{-4}$  mole/0.1 g of trunk polymer.

### Preparation of Trunk Polymer Containing —COONa or —SO<sub>3</sub>Na

Trunk polymers, as 100–200 mesh powders, containing —COOH or —SO<sub>3</sub>H were carefully neutralized by an equivalent aqueous NaOH solution.

### Preparation of Trunk Polymer Containing



A 100–200 mesh powder of trunk polymer containing —COOH or SO<sub>3</sub>H was soaked into a small excess of ammoniac water of pyridine–benzene solution for 24 hr, and then excess alkali and solvent were evaporated. These trunk polymers were dried under vacuum at 98°C for 2 hr.

### Procedure of Graft Copolymerization

βPL was graft-copolymerized by the methods described in the previous paper.<sup>2</sup>

### Separation of Graft Copolymer

The crude product was extracted by a 20-fold volume of chloroform at 60°C for 3 hr. The mixture of βPL homopolymer and the St–DVB copolymer was separated completely by this method (Table II). The per cent grafting was determined from weight increase of trunk polymer.

TABLE II  
Chain Transfer to Trunk Polymer (ST–DVB copolymer)  
and Efficiency of Extraction of P-βPL from Trunk Polymer<sup>a</sup>

Expt no.	Catalyst	Time, hr	Conversion, %	Graft copolymer, g	Grafting, %
G3-1	CH <sub>3</sub> SO <sub>3</sub> H	7	96.2	0.1011	1.1
G3-5	CH <sub>3</sub> COONa	54	32.2	0.0930	±0

<sup>a</sup> ST–DVB copolymer, 100 mg; catalyst,  $4.38 \times 10^{-4}$  mole; βPL, 1 cc; toluene, 4 cc; 60°C; *in vacuo*.

### Determination of Carboxyl Group and Sulfoxyl Group in the Trunk Polymer

A 12-cc portion of 0.1*N* sodium methoxide–ethanol solution was added to 0.1 g of 100–200 mesh polymer swollen in 10 cc of chloroform and it was back-titrated with 0.1*N* hydrochloric acid, phenolphthalein being used as an indicator.

## RESULTS

Graft Copolymerization of  $\beta$ PL onto Trunk Polymer Containing —COOK

The trunk polymer containing —COOK has the highest activity in anionic systems. The total conversion was observed to be ca. 85% at 60°C for 10 hr as shown in Figure 1, and it is ca. 4 times that of the trunk polymer containing —COONa. Grafting efficiency is comparably high (70–60%) and decreases with reaction time.

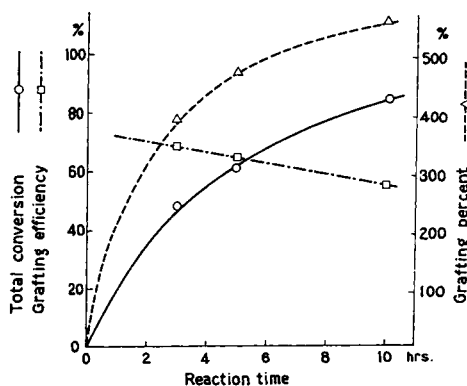


Fig. 1. Graft copolymerization in toluene of  $\beta$ PL onto trunk polymer containing COOK. Trunk polymer, 100 mg; COOK in trunk polymer,  $4.54 \times 10^{-4}$  mole;  $\beta$ PL, 1 cc; toluene, 4 cc; 60°C; *in vacuo*.

Graft Copolymerization of  $\beta$ PL onto Trunk Polymer Containing —COONa

The results of the graft copolymerization of  $\beta$ PL onto the trunk polymer containing —COONa are presented in Figure 2. The rate of polymeriza-

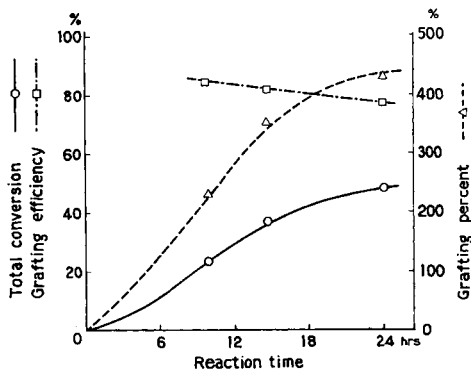


Fig. 2. Graft copolymerization in toluene of  $\beta$ PL onto trunk polymer containing COONa. COONa content in trunk polymer,  $4.54 \times 10^{-4}$  mole; other conditions as in Fig. 1.

tion by the trunk polymer containing  $-\text{COONa}$  is second only to that of polymer containing  $-\text{COOK}$ . Grafting efficiency is quite high, i.e., ca. 80%.

### Graft Copolymerization of $\beta\text{PL}$ onto Trunk Polymer Containing $-\text{COONH}_4$

$\beta\text{PL}$  was graft-copolymerized onto trunk polymer containing  $-\text{COONH}_4$ , which is the product of a weak acid and a weak base (Fig. 3). Ammonium carboxylate group hardly dissociates and therefore the rate of polymerization is very low, one tenth of that with  $-\text{COONa}$ . However, the grafting efficiency is the third highest of all catalysts used, following  $-\text{COOK}$  and  $-\text{COONa}$ .

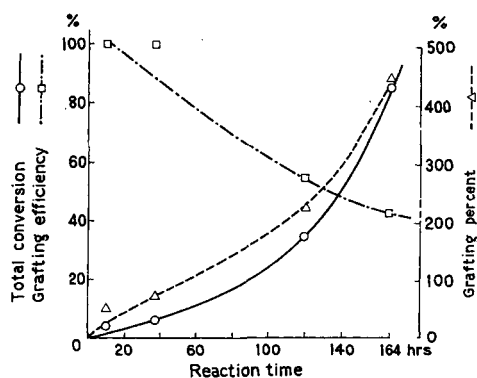


Fig. 3. Graft copolymerization in toluene of  $\beta\text{PL}$  onto trunk polymer containing  $\text{COONH}_4$ .  $\text{COONH}_4$  in trunk polymer,  $4.54 \times 10^{-4}$  mole; other conditions as in Fig. 1.

### Graft Copolymerization of $\beta\text{PL}$ onto Trunk Polymer Containing $-\text{COOH}$

$\beta\text{PL}$  was graft-copolymerized onto trunk polymer containing  $-\text{COOH}$ , which is a weak acid (Table III). The rate of polymerization was the lowest of all catalysts used. The total conversion was limited to  $\sim 5\%$  at  $60^\circ\text{C}$  for 768 hr and about 44% at  $120^\circ\text{C}$  for 120 hr. The rate of polymerization is low, because the carboxyl group dissociates only very slightly. The grafting efficiency in the case of  $-\text{COOH}$  was slightly lower than that of  $-\text{COONH}_4$  and was markedly higher than that of  $-\text{SO}_3\text{Na}$ .

### Graft Copolymerization of $\beta\text{PL}$ onto Trunk Polymer Containing $-\text{SO}_3\text{Na}$

$\beta\text{PL}$  was graft copolymerized onto the trunk polymer containing  $-\text{SO}_3\text{Na}$  which is the product of strong acid and strong base (Fig. 4). A very long induction period was observed, and the plot of conversion against reaction time showed considerable scatter. The rate of polymerization is very much

TABLE III  
Graft Copolymerization of  $\beta$ PL onto Trunk Polymer Containing COOH<sup>a</sup>

Expt no.	Polymerization system	$\beta$ PL, cc	Toluene, cc	Temp, °C	Time, hr	Total conversion, %	Grafting, %	Grafting efficiency, %
G8-24	In toluene	1	4	60	7	0	—	—
G8-25	"	"	"	"	240	0.18	1.5	71.5
G8-26	"	"	"	"	768	2.1 (4.8) <sup>b</sup>	19.6	82.3 (35.3) <sup>b</sup>
G25-6	"	"	"	80	48	0.43	5.0	83.0
G54-1	"	"	"	120	3	1.08 (1.18) <sup>b</sup>	12.2	97.6 (89.0) <sup>b</sup>
G54-2	"	"	"	"	25	6.51 (7.63) <sup>b</sup>	74.6	99.1 (84.4) <sup>b</sup>
G54-3	"	"	"	"	120	25.3 (43.5) <sup>b</sup>	241.3	82.4 (47.9) <sup>b</sup>
G18-2	In bulk	3	—	60	24	0.49	15.3	90.0
G18-1	"	"	—	"	120	1.1	37.0	98.4
G18-3	"	"	—	"	264	2.1	69.0	94.2
G18-4	"	"	—	"	360	2.7	92.1	98.3

<sup>a</sup> Trunk polymer, 100 mg; COOH in trunk polymer,  $4.54 \times 10^{-4}$  mole; *in vacuo*.

<sup>b</sup> Unreactive monomer was removed to evaporate from crude product in reducing pressure.

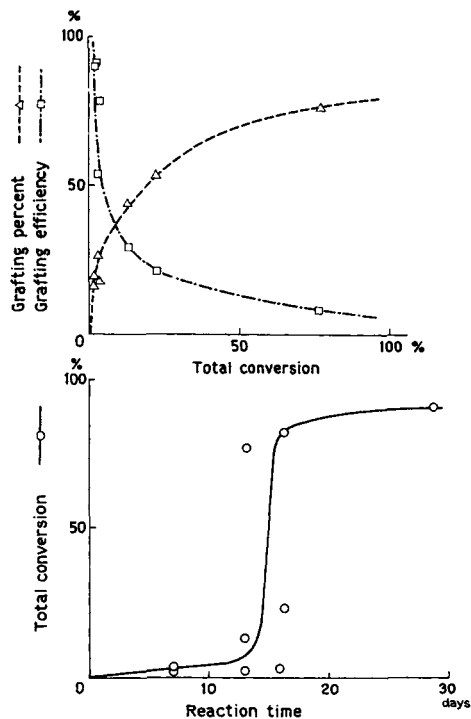


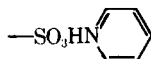
Fig. 4. Graft copolymerization in toluene of  $\beta$ PL onto trunk polymer containing  $\text{SO}_3\text{Na}$ .  $\text{SO}_3\text{Na}$  in trunk polymer,  $4.38 \times 10^{-4}$  mole; other conditions as in Fig. 1.

slower than those of  $\text{—SO}_3\text{HN=CH—CH=CH—CH=CH}$  or  $\text{—SO}_3\text{H}$ . The induction period corresponds to the period in which acrylic acid produced from  $\beta$ PL accumulates or the addition product of  $\beta$ PL with  $\text{—SO}_3\text{Na}$  is produced as shown in eq. (1).

#### Graft Copolymerization of $\beta$ PL onto Trunk Polymer Containing $\text{—SO}_3\text{NH}_4$

Graft copolymerization of  $\beta$ PL onto the trunk polymer containing  $\text{—SO}_3\text{NH}_4$ , which is the product of a strong acid and a weak base, was carried out (Fig. 5).  $\beta$ PL is polymerized relatively fast after a long induction period, in the same manner as grafting onto the trunk polymer containing  $\text{—SO}_3\text{Na}$ . The grafting efficiency decreases rapidly in the initial period of polymerization up to about 20% and is lower than that of  $\text{—SO}_3\text{Na}$ .

#### Graft Copolymerization of $\beta$ PL onto Trunk Polymer Containing



The results of the graft copolymerization onto the trunk polymer containing  $\text{SO}_3\text{HN=CH—CH=CH—CH=CH}$  are shown in Figure 6. The



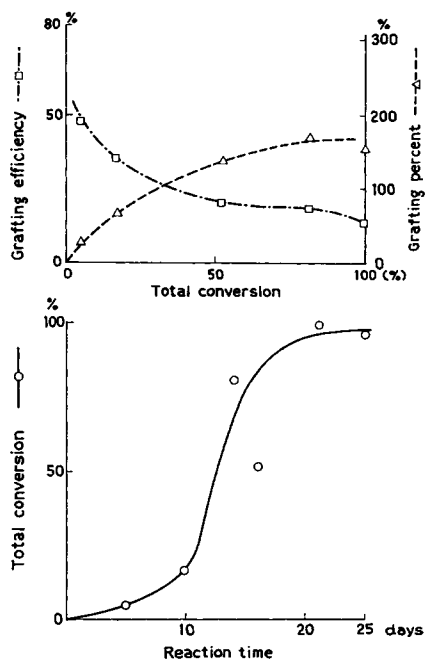


Fig. 5. Graft copolymerization in toluene of  $\beta$ PL onto trunk polymer containing  $\text{SO}_3\text{-NH}_4$ .  $\text{SO}_3\text{NH}_4$  in trunk polymer,  $4.38 \times 10^{-4}$  mole; other conditions as in Fig. 1.

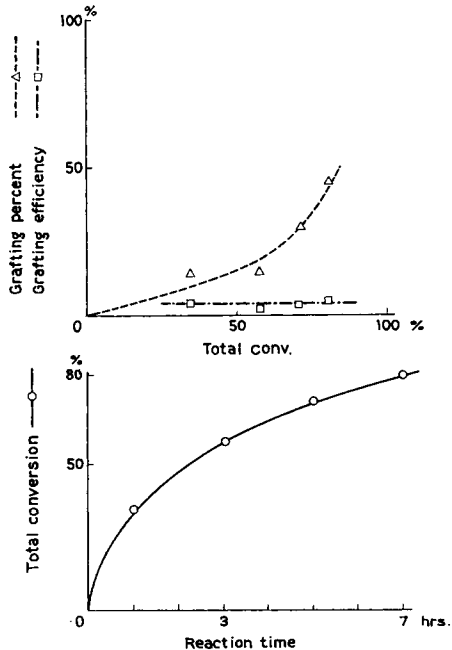


Fig. 6. Graft copolymerization in toluene of  $\beta$ PL onto the trunk polymer containing  $\text{SO}_3\text{NH-CHCH=CHCH=CH}$ .  $\text{SO}_3\text{HN-CHCH=CHCH=CH}$  in trunk polymer,  $4.38 \times 10^{-4}$  mole; other conditions as in Fig. 1.

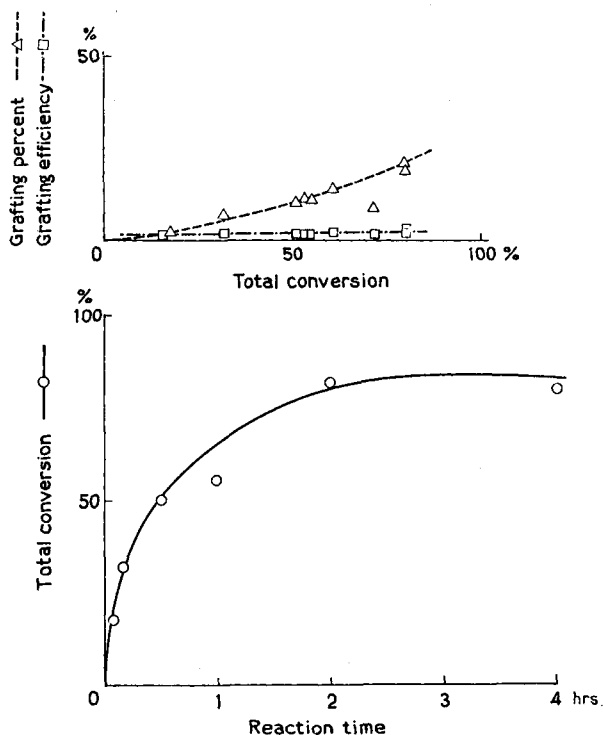


Fig. 7. Graft copolymerization in toluene of  $\beta$ PL onto trunk polymer containing  $\text{SO}_3\text{H}$ , Trunk polymer, 100 mg;  $\text{SO}_3\text{H}$  in trunk polymer,  $4.38 \times 10^{-4}$  mole;  $\beta$ PL, 1 cc; toluene, 4cc;  $60^\circ\text{C}$ ; in nitrogen.

rate of polymerization is as fast as that in the case of  $-\text{SO}_3\text{H}$ . The grafting efficiency is very low and hardly varies with increase of total conversion.

#### Graft Copolymerization of $\beta$ PL onto Trunk Polymer Containing $-\text{SO}_3\text{H}$

The results of the graft copolymerization onto trunk polymer containing  $-\text{SO}_3\text{H}$  are shown in Figure 7. Sulfonic acid is a typical cationic catalyst and the rate of polymerization is the fastest in all catalysts used. The conversion is saturated at about 80% in the same manner as the homopolymerization of  $\beta$ PL by toluenesulfonic acid as shown in our previous paper.<sup>1</sup> The grafting efficiency is very low and is not varied by an increase of total conversion. A small amount of graft copolymer is produced by recombination between growing chain end and counteranion.

#### Comparison among Graft Copolymerizations of $\beta$ PL by Various Catalysts in Toluene

Total conversion, per cent grafting, and grafting efficiency for the graft copolymerization of  $\beta$ PL onto trunk polymers containing various carboxylates are compared in Figures 8–10. The order of total conversion

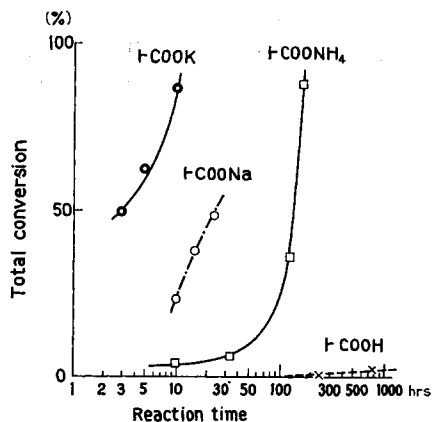


Fig. 8. Comparison of total conversion in graft copolymerization of  $\beta$ PL onto various carboxylated trunk polymers.

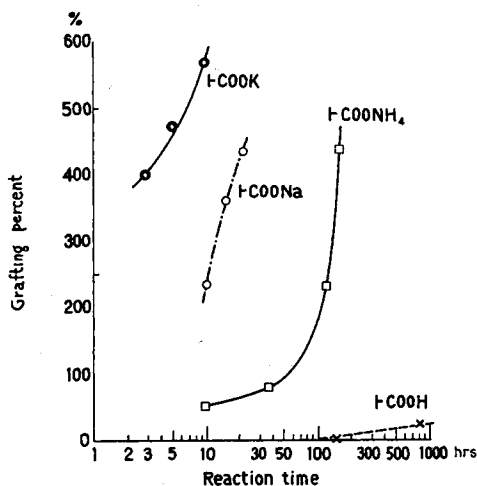
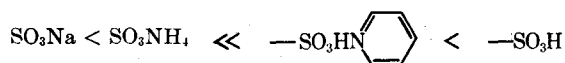
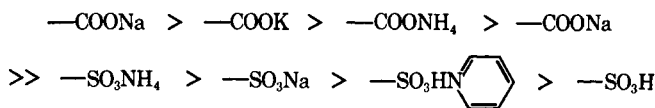


Fig. 9. Comparison of per cent grafting in graft copolymerization of  $\beta$ PL onto various carboxylated trunk copolymers.

and per cent grafting in the case of acetate catalyst is  $-\text{COOK} > -\text{COONa} > -\text{COONH}_4 > -\text{COOH}$ ; the carboxylate containing the lower electrophilic cation favors the higher polymerization activity. It has been reported<sup>4,5</sup> that the catalyst containing lower electrophilic cation has higher polymerization activity in the polymerization of  $\beta$ PL by the catalyst such as hydroxide, carbonate, acetate, or alkali halide. The total conversion and per cent grafting in the case of sulfonate catalysts (Figs. 11–13) decreases in the order



and this order coincides with the order of cationic polymerization activity; the sulfonate containing the more electrophilic cation favors higher polymerization activity in the reverse order of that for carboxylate. The order of grafting efficiency for the nature of catalyst is



This order coincides almost with that of anionic activity. These results are summarized in Figure 14.

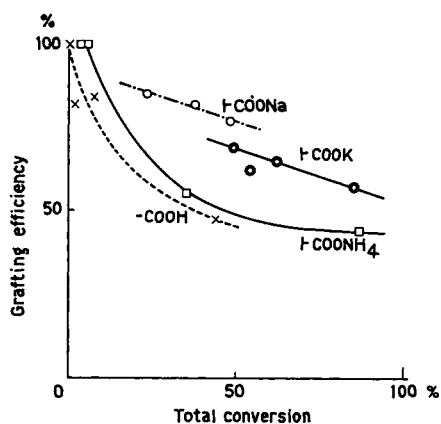


Fig. 10. Relationship between total conversion and grafting efficiency in the graft copolymerization of  $\beta$ PL onto various carboxylated trunk polymers.

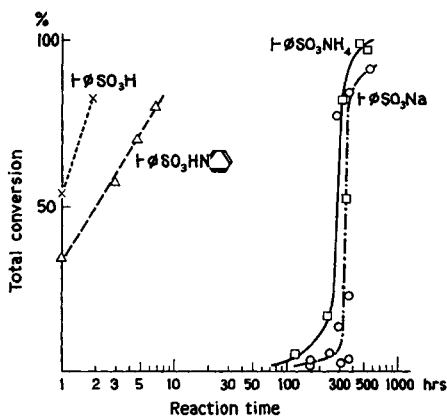


Fig. 11. Comparison of total conversion on the graft copolymerization of  $\beta$ PL onto various sulfonated trunk polymers.

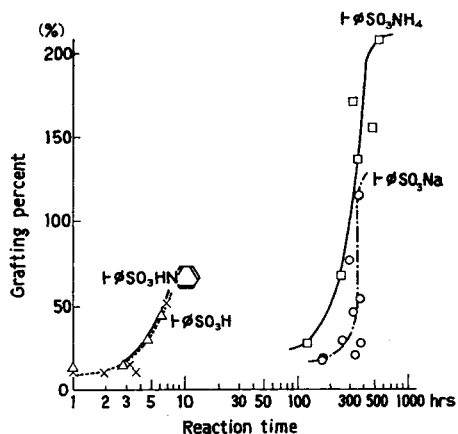


Fig. 12. Comparison of per cent grafting in the graft copolymerization of  $\beta$ PL onto various sulfonated trunk polymers.

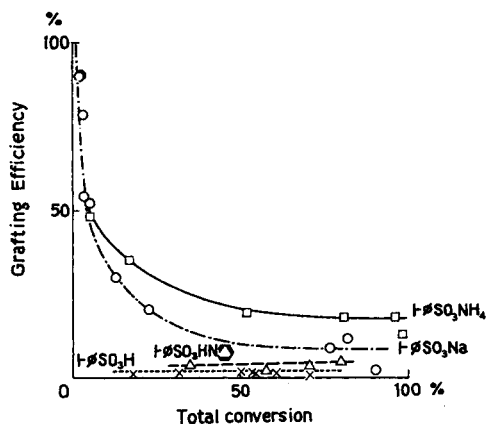


Fig. 13. Relationship between total conversion and grafting efficiency in graft copolymerization of  $\beta$ PL onto various sulfonated trunk polymers.

	$\text{fCOOK}$	$\text{fCOONa}$	$\text{fCOONH}_4$	$\text{fCOOH}$	$\text{f-}\phi\text{SO}_3\text{Na}$	$\text{f-}\phi\text{SO}_3\text{NH}_4$	$\text{f-}\phi\text{SO}_3\text{HN}$	$\text{f-}\phi\text{SO}_3\text{H}$
Order of basicity	←							
Order of polymerization activity	anionic ← → cationic							
Order of total conversion	High	High	High	Low	Low	Low	High	High
Order of grafting percent	High	High	High	Low	Low	Low	High	High
Order of grafting efficiency	High	High	High	Low	Low	Low	High	High

Fig. 14. Summary of graft copolymerization of  $\beta$ PL onto various trunk polymers.

### Graft Copolymerization in Bulk of $\beta$ PL onto Trunk Polymer Containing $-\text{SO}_3\text{Na}$

In our previous paper,<sup>1</sup> it was found that no acrylic acid is produced from  $\beta$ PL in toluene but that the reaction proceeds easily in bulk, and the rate of polymerization of  $\beta$ PL by sodium sulfonate is accelerated in the presence of acrylic acid. Therefore, the behaviors of graft copolymerization of  $\beta$ PL onto the trunk polymer containing  $-\text{SO}_3\text{Na}$  in bulk and in toluene was compared.

The rate of polymerization in bulk (Table IV) is much faster than that in

TABLE IV  
Graft Copolymerization in Bulk of  $\beta$ PL onto Trunk Polymer Containing  $\text{SO}_3\text{Na}$ <sup>a</sup>

Expt no.	Time, hr	Total conversion, %	Grafting, %	Grafting efficiency, %
G69-1	24	7.23	0.5	0.199
G69-2	48	10.7	4.9	1.31
G69-4	63	13.6	4.5	0.954
G69-3	191	41.7	16.5	1.14

<sup>a</sup> Trunk polymer, 0.1 g;  $-\text{SO}_3\text{Na}$  in trunk polymer,  $4.38 \times 10^{-4}$  mole;  $\beta$ PL, 3cc; 60°C, *in vacuo*.

toluene (Fig. 4). The grafting efficiency in bulk is limited to about 1%, independent of the total conversion, but in toluene the efficiency is rather high and decreases with increasing total conversion. These results demonstrate that the mechanism of initiation by the addition product between  $\beta$ PL and  $-\text{SO}_3\text{Na}$  predominates in toluene, but the mechanism of initiation by cation exchange [eq. (2)] between  $-\text{SO}_3\text{Na}$  and acrylic acid predominates in bulk.

### Comparison of Polymerization Activity of Liquid Phase Separated from Trunk Polymer and That in Contact with Trunk Polymer after Partial Reaction

$\beta$ PL was polymerized by the trunk polymer up to a suitable conversion in the first step polymerization, and then the liquid is separated from trunk polymer. The liquid in contact with trunk polymer was separately polymerized in a second step polymerization (Fig. 15). The results of the two-step polymerization by the four representative trunk polymers containing  $-\text{COONa}$ ,  $-\text{COOH}$ ,  $-\text{SO}_3\text{Na}$ , or  $-\text{SO}_3\text{H}$  are shown in Figure 16 and Table V. The conversions were determined from the weight of the residues after removal of unreacted monomer by evaporation.

In the case of the anionic graft copolymerization of  $\beta$ PL with trunk polymer containing  $-\text{COONa}$ , a higher polymerization activity is observed in both the liquid phase separated from the trunk polymer and the liquid phase in contact with the trunk polymer. It has been reported<sup>6</sup> that sodium acrylate is produced by chain transfer of growing chain end to

TABLE V  
Comparison of Polymerization Activity of the Liquid Phase Separated from Trunk Polymer and that in Contact with Trunk Polymer

Expt no.	Trunk polymer	Temp, °C		Time, hr		Conversion, %			
		1st	2nd	1st	2nd	Phase containing trunk polymer		Phase separated from trunk polymer	
						1st (T <sub>1</sub> )	2nd (T <sub>2</sub> )	1st (L <sub>1</sub> )	2nd (L <sub>2</sub> )
G68-1	—COONa	60	60	1	18	8.24	85.5	1.88	75.3
2	—COOH	60	60	168	280	4.95	76.2	1.79	19.02
5	—vSO <sub>3</sub> Na	60	60	74	137	16.3	94.4	15.07	16.35
4	—vSO <sub>3</sub> H	26	60	1/60	90	5.45	Ex-	2.79	8.14
							pl-		
							sive		

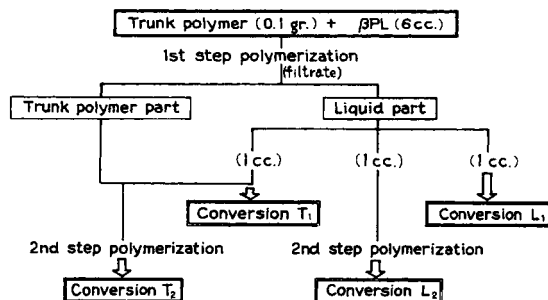


Fig. 15. Polymerization activity of liquid phase separated from trunk polymer. Flow sheet for two-step polymerization.

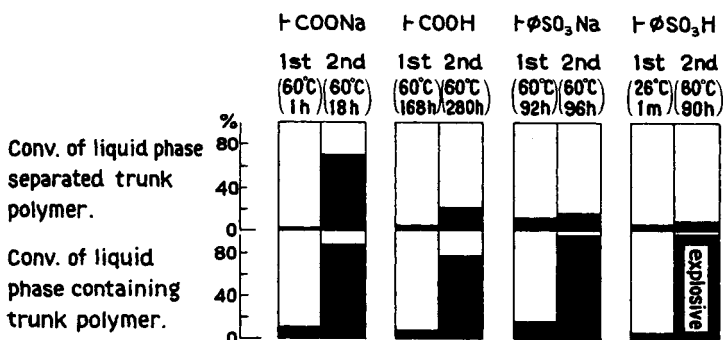


Fig. 16. Comparison of polymerization activity of liquid phase separated from trunk polymer and that in contact with trunk polymer.

monomer in the anionic polymerization of  $\beta$ PL. In the graft copolymerization onto trunk polymer containing  $-\text{COONa}$ , the growing chain end of the graft copolymer participates in chain transfer to monomer, and the sodium acrylate initiates polymerization of  $\beta$ PL in the liquid phase separated from the trunk polymer. In the case of graft copolymerization onto trunk polymer containing  $-\text{COOH}$ , polymerization is observed in both the liquid phase and the trunk polymer phase in the same manner as grafting onto trunk polymer containing  $-\text{COONa}$ . In the case of the grafting onto

TABLE VI  
Hydrolysis of the Graft Copolymer of  $\beta$ PL on Trunk Polymer Containing  $\text{SO}_3\text{H}$

Expt no.	Grafting, %		
	Original graft copolymer	Extract in $\text{CHCl}_3$ at $60^\circ\text{C}$ for 16 hr	Hydrolyzed by hydrated $\text{CHCl}_3$ at room temperature for 24 hr
G4-30	28.5	25.5	12.2
G4-31	66.8	60.3	15.7



TABLE VII  
Graft Copolymerization by Means of Chain Termination of Growing Cation onto COO<sup>-</sup> in Trunk Polymer<sup>a</sup>

Expt no.	Trunk polymer, g	$\beta$ PL, cc	Toluene, cc	CH <sub>3</sub> SO <sub>3</sub> H, mole	Conversion, %	Grafting, %	Grafting efficiency, %
G51-1	0.15 (containing COOH)	1.5	6	$6.6 \times 10^{-3}$	50.5	7.1	1.21
G51-3	0.1257 (containing COONa)	"	"	"	54.3	35.3	4.71

<sup>a</sup> COO<sup>-</sup> in trunk polymer,  $6.6 \times 10^{-4}$  mole/0.15 g; in N<sub>2</sub>, 60°C; 3 hr.

trunk polymer containing  $-\text{SO}_3\text{Na}$ , the liquid phase separated from the trunk polymer shows almost no polymerization of  $\beta\text{PL}$ , and polymerization occurs chiefly on the surface of the trunk polymer. In the case of graft copolymerization onto trunk polymer containing  $-\text{SO}_3\text{H}$ , polymerization proceeds explosively only on the surface of trunk polymer and does not proceed in the liquid phase separated from trunk polymer.

### **Hydrolysis of Graft Copolymer of $\beta\text{PL}$ onto Trunk Polymer Containing $-\text{SO}_3\text{H}$**

A small amount of graft copolymer is obtained also in the graft copolymerization of  $\beta\text{PL}$  onto the trunk polymer containing  $-\text{SO}_3\text{H}$ . Graft copolymerization by chain transfer to St and DVB units could not be observed as shown in Table II (experiment G3-1). Therefore, the branch polymers are supposed to be attached to the trunk polymer by the sulfonic ester bond which is easily hydrolyzed by water. This is proved by the fact that the per cent grafting does not decrease on repeated extraction with purified chloroform at  $60^\circ\text{C}$  for 16 hr, but does decrease markedly on extraction in hydrated chloroform at room temperature for 24 hr (Table VI).

### **Graft Copolymerization of $\beta\text{PL}$ by Chain Termination of Growing Cation onto the Carboxyl Anion in Trunk Polymer**

Both possibilities, i.e., an anionic mechanism and a cationic mechanism, are considered in the graft copolymerization onto the trunk polymer containing  $-\text{COOH}$  as described in our previous paper.<sup>1</sup> Graft copolymer is undoubtedly produced by the anionic mechanism with carboxyl anion; however, the possibility of cationic polymerization with chain termination of growing cation onto carboxyl anion remains. To confirm this possibility,  $\beta\text{PL}$  was polymerized with toluenesulfonic acid catalyst in the presence of trunk polymers containing  $-\text{COOH}$  or  $-\text{COONa}$  (Table VII). A small amount of graft copolymer was produced, and the grafting efficiency was very low.

## **DISCUSSION**

### **Some Factors Affecting the Grafting Efficiency**

The main influence on the grafting efficiency is whether graft copolymerization proceeds by a cationic mechanism or an anionic mechanism.

In the case of anionic graft copolymerization, the grafting efficiency is decreased by the following secondary reactions: chain transfer to monomer, solvent, or impurity; formation of active species separated from trunk polymer; cationic polymerization which proceeds simultaneously.

In the cationic graft copolymerization, the grafting efficiency is increased by the following secondary reactions: chain transfer to the trunk polymer; recombination of growing cation with anion in the trunk polymer; anionic

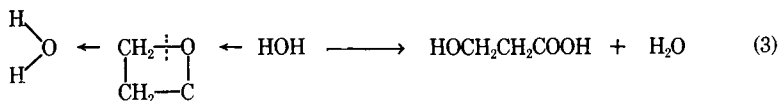
polymerization which proceeds simultaneously by anions on the trunk polymer.

In the anionic grafting, chain transfer hardly occurs in toluene, as shown in our previous paper,<sup>2,3</sup> but it is not negligible. The active species produced by cation exchange between sodium sulfonate and acrylic acid become independent of the trunk polymer, and homopolymer is produced by these active species. The two possibilities of cationic mechanism and anionic mechanism are considered in the grafting onto the trunk polymer containing —COOH. For the secondary chain transfer to trunk polymer in cationic polymerization, the graft copolymerization by chain transfer to DVB and St units in the trunk polymer may be neglected, as shown in Table II. Graft copolymerization by recombination of growing cation end with sulfonate anion or carboxyl anion in the trunk polymer is observed, but the grafting efficiency is very low.

Grafting efficiency at the same conversion decreases gradually, being highest for anionic-active trunk polymer and least for cationic trunk polymer. In general, grafting efficiencies in the case of carboxylated trunk polymers are quite high, but grafting efficiencies in the case of sulfonated trunk polymers are very low. These results demonstrate that anionic mechanisms predominate in the grafting onto the carboxylated trunk polymers and cationic mechanisms predominate in grafting onto the sulfonated polymer.

### Mechanism of Polymerization of $\beta$ PL by Covalent Neutral Catalyst

A typical covalent neutral catalyst is water. The reaction of  $\beta$ PL with water, that is, hydrolysis of  $\beta$ PL, has been investigated in detail.<sup>7,8,10</sup>  $\beta$ PL is reacted with water by a "push-pull" reaction<sup>7</sup> as shown in eq. (3):



In this reaction, water reacts with  $\beta$ PL as both acid and base.

Carboxylic acid is a weak acid and is closest to a covalent neutral catalyst of all the catalysts used. It has been reported<sup>9</sup> but not in detail, that  $\beta$ PL reacts with acetic acid with the use of concentrated  $\text{H}_2\text{SO}_4$  as catalyst. The band corresponding to carboxylic acid anhydride is not observed in the infrared spectrum of P- $\beta$ PL catalyzed by  $\text{CH}_3\text{COOH}$ , and grafting efficiency is quite high in grafting onto trunk polymer containing —COOH. These results demonstrate that the anionic mechanisms predominate in the polymerization with carboxylic acid.

### Mechanisms of Polymerization of $\beta$ PL by Ionic Neutral Catalysts

The reactions of  $\beta$ PL with salts have been investigated in detail in studies of the salt effect in the hydrolysis of  $\beta$ PL.<sup>10,11</sup>

It has been reported<sup>12-14</sup> that sodium salts of  $\beta$ -substituted propionates are produced by reaction of  $\beta$ PL with various salts such as NaCl, NaBr, NaHS, Na<sub>2</sub>S, Na<sub>2</sub>S<sub>2</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, NaNO<sub>2</sub>, NaCN, NaSCN, C<sub>6</sub>H<sub>5</sub>-SO<sub>2</sub>Na, and RCOONa. By analogy with these reactions, sodium  $\beta$ -sulfoxypropionate should be produced by the reaction of  $\beta$ PL with sodium sulfonate as shown by eq. (1), and polymerization should be initiated by this compound. However, the accelerating effect caused by the formation of acrylic acid complicates the polymerization of  $\beta$ PL by sodium sulfonate as shown by eq. (2). No acrylic acid is produced from  $\beta$ PL in toluene but it is produced easily in bulk; therefore the grafting efficiency in toluene is higher than that in bulk. These results indicate that the mechanism shown by eq. (1) predominates in toluene, and that shown by eq. (2) predominates in bulk.

### CONCLUSIONS

Graft copolymerization of  $\beta$ PL onto trunk polymers containing a series of catalytic groups from anionic to cationic (Table I) was carried out. The carboxylated trunk polymer containing a less electrophilic cation favors higher polymerization activity. On the other hand, the sulfonated trunk polymer, which contains a more electrophilic cation, shows higher polymerization activity. In general, grafting efficiency onto carboxylated trunk polymers is higher than that onto sulfonated trunk polymers. The order of grafting efficiency for the nature of catalyst almost coincides with that of anionic activity of catalyst. In the graft copolymerization onto trunk polymer containing —COOH, an anionic mechanism predominates. On the other hand, in the graft copolymerization onto trunk polymer containing SO<sub>3</sub>Na, two initiation mechanisms are proposed, as shown by eqs. (1) and (2).

The authors wish to express their thanks to Dr. S. Tazuke for helpful discussions.

### References

1. T. Shiota, K. Hayashi, and S. Okamura, *J. Appl. Polym. Sci.*, in press.
2. T. Shiota, Y. Goto, and K. Hayashi, *J. Appl. Polym. Sci.*, **11**, 773 (1967).
3. T. Shiota, Y. Goto, and K. Hayashi, *J. Appl. Polym. Sci.*, **11**, 753 (1967).
4. S. Okamura, T. Higashimura, and A. Tanaka, *Kogyo Kagaku Zasshi*, **65**, 707 (1962).
5. S. Ikeda, S. Tazuke, and S. Okamura, unpublished data.
6. Y. Yamashita, Y. Ishikawa, T. Tsuda, and S. Miura, *Kogyo Kagaku Zasshi*, **66**, 104 (1963).
7. A. R. Olson and R. J. Miller, *J. Amer. Chem. Soc.*, **60**, 2687 (1938).
8. A. R. Olson and J. L. Hyde, *J. Amer. Chem. Soc.*, **63**, 2459 (1941).
9. T. L. Gresham, J. E. Jansen, and F. W. Shaver, *J. Amer. Chem. Soc.*, **72**, 72 (1950).
10. F. A. Long and Mary Purchase, *J. Amer. Chem. Soc.*, **72**, 3267 (1950).
11. A. R. Olson and P. V. Youle, *J. Amer. Chem. Soc.*, **73**, 2468 (1951).
12. T. L. Gresham, J. E. Jansen, F. W. Shaver, and J. T. Gregory, *J. Amer. Chem. Soc.*, **70**, 999 (1948).

13. T. L. Gresham, J. E. Jansen, F. W. Shaver, M. R. Frederick, F. T. Fiedorek, R. A. Bankert, J. T. Gregory, and W. L. Beears, *J. Amer. Chem. Soc.*, **74**, 1323 (1952).

14. T. L. Gresham, J. E. Jansen, and F. W. Shaver, *J. Amer. Chem. Soc.*, **70**, 1003 (1948).

Received March 4, 1968