

## Ionic Graft Copolymerization. III. Graft Copolymerization of $\beta$ -Propiolactone onto Polyacrylonitrile Containing Diketene Units

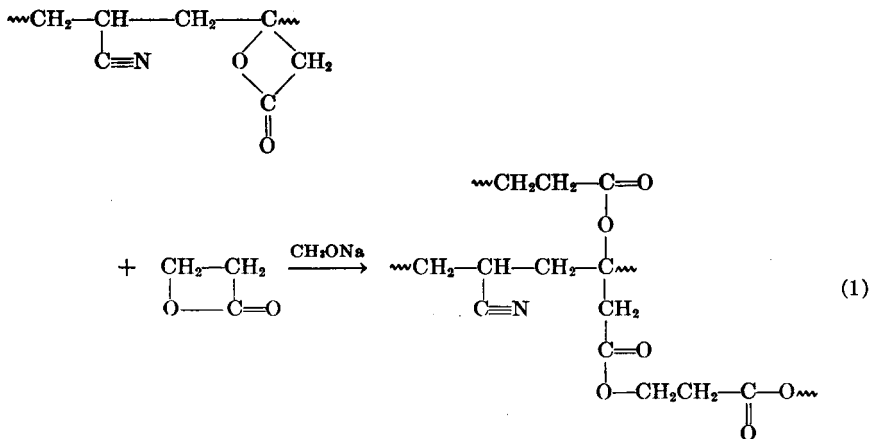
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### Synopsis

Polyacrylonitrile (PAN)- $\beta$ -propiolactone ( $\beta$ PL) graft copolymer was synthesized by means of the ionic polymerization of  $\beta$ PL in the presence of polyacrylonitrile containing diketene units by using basic catalysts. A graft copolymer was produced by the copolymerization of  $\beta$ PL with the lactone ring in the trunk polymer. In this graft copolymerization method, the grafting efficiency was low. However, grafting efficiency increased with the mole ratio of polymeric lactone to  $\beta$ PL; also higher molecular weight of P $\beta$ PL favored higher grafting efficiency. The reactivity ratio of polymeric lactone to  $\beta$ PL was estimated to be in the range of 0.1-0.3.

### INTRODUCTION

Polyacrylonitrile (PAN)- $\beta$ -propiolactone ( $\beta$ PL) graft copolymer was synthesized by means of ionic polymerization in which  $\beta$ PL was copolymerized with lactone contained in a polyacrylonitrile trunk polymer containing diketene (DK) through the use of basic catalysts as shown in eq. (1):



Factors which influence the grafting efficiency are: (1) the reactivity ratio of DK (lactone) unit in trunk polymer to  $\beta$ PL; (2) the mole ratio of DK unit to  $\beta$ PL in the reaction system; (3) the molecular weight of P $\beta$ PL produced.

In most studies,  $\beta$ PL has been desiccated with calcium hydride, sodium sulfate, or toluylene diisocyanate, but it was found that it could not be purified sufficiently by these desiccating agents.<sup>1</sup> It was found that  $\beta$ PL was desiccated perfectly by passing it over calcium chloride quickly and by distillation.<sup>1</sup> With the use of  $\beta$ PL dried by the former method, the molecular weight of homopolymer was very low and the grafting efficiency was also very low, almost independent of the reaction time.

On the other hand, when  $\text{CaCl}_2$  was used as desiccant for monomer, the grafting efficiency and molecular weight of homopolymer increased with reaction time.

The grafting efficiency was correlated with the mole ratio of DK to  $\beta$ PL and the molecular weight of the homopolymer. The reactivity ratios  $r_1$  and  $r_2$  estimated from the graft copolymer composition curve were 0.1–0.3 and 3.6–9.1 for the polymer lactone and  $\beta$ PL, respectively.

$\beta$ PL was grafted on to poly(methyl methacrylate) (PMMA) trunk polymer containing DK.

In this case, the grafting efficiency was high by reason of chain transfer to MMA unit in the trunk polymer.

## EXPERIMENTAL

### Reagents

**Trunk Polymer.**<sup>2</sup> PAN trunk polymer and PMMA trunk polymer were prepared by radical copolymerization of DK-AN or DK-MMA at 60°C.

**$\beta$ PL.**  $\beta$ PL was obtained from Dainihon Celluloid Co., passed quickly over calcium chloride two times, and followed by distillation at reduced pressure. The water content of the  $\beta$ PL obtained in this way was less than 10 ppm.

**Sodium Methylate.** Absolute methanol was reacted with sodium metal, and recrystallized from absolute methanol.

### Method of Graft Copolymerization

Sodium methylate ( $3.3 \times 10^{-5}$  mole) and 100 mg. of trunk polymer were dried in a reaction tube at 98°C. under reduced pressure ( $10^{-4}$  mm. Hg) for 3 hr. and 3 ml. of  $\beta$ PL was added to the reaction tube in dry box. The reaction tube was then evacuated by using a high-vacuum technique ( $10^{-4}$  mm. Hg).

### Separation of Graft Copolymer

Graft copolymer on PAN was separated by chloroform extraction. Graft copolymers on PMMA were separated by toluene extraction (Fig. 1).

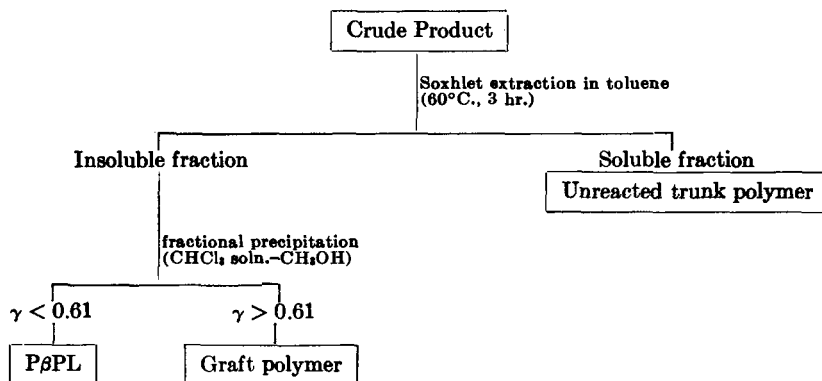


Fig. 1. Separation of PMMA- $\beta$ PL graft copolymer from crude product.

Mixtures of P $\beta$ PL and these trunk polymers were separated completely by these methods.

The per cent grafting was determined gravimetrically.

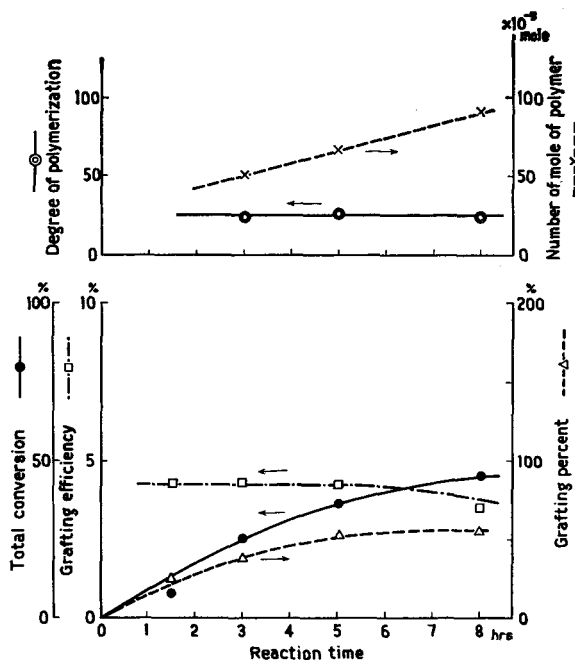


Fig. 2. Grafting of  $\beta$ PL purified with  $\text{Na}_2\text{SO}_4$ : (●) degree of polymerization; (×) number of moles of polymer; (○) total conversion; (□) grafting efficiency; (△) per cent grafting.  $[\text{DK}]_0/[\beta\text{PL}]_0$ , 4.6/1000 (molar); trunk polymer, 100 mg. (DK, 12.0 mole-%);  $\beta$ PL, 3.0 cc.;  $\text{CH}_3\text{ONa}$ ,  $3.3 \times 10^{-5}$  mole;  $60^\circ\text{C}$ .; in air.

## RESULTS

## Effect of Reaction Time

$\beta$ PL was grafted at 60°C. by sodium methylene onto PAN trunk polymer containing 12% DK. Total conversion and per cent grafting increased with reaction time. When  $\beta$ PL purified with calcium chloride was used (Fig. 2), the molecular weight of P $\beta$ PL produced increasingly steadily with reaction time and grafting efficiency also increased as a function of molecular

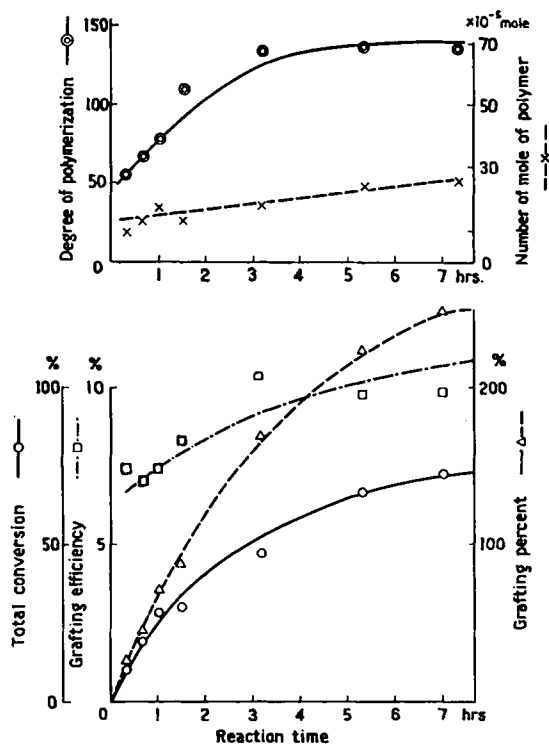


Fig. 3. Grafting of  $\beta$ PL purified by  $\text{CaCl}_2$ : (⊗) degree of polymerization; (×) number of moles of polymer; (○) total conversion; (□) grafting efficiency; (△) per cent grafting.  $[\text{DK}]_0/[\beta\text{PL}]_0$ , 4.6/1000 (molar); trunk polymer, 100 mg. (DK, 12.5 mole-%);  $\beta$ PL, 3.0 cc.;  $\text{CH}_3\text{ONa}$ ,  $3.3 \times 10^{-3}$  mole; 60°C.; *in vacuo*.

weight of P $\beta$ PL. On the other hand, the results for  $\beta$ PL purified with  $\text{Na}_2\text{SO}_4$  (shown in Fig. 3) indicated that the degree of polymerization of P $\beta$ PL produced and grafting efficiency were very low, about 25 and 4%, respectively.

This difference may be attributed to chain transfer to impurity.

A higher DK/ $\beta$ PL mole ratio would favor higher grafting efficiency. The experiment in Figure 4 was attempted at a threefold concentration

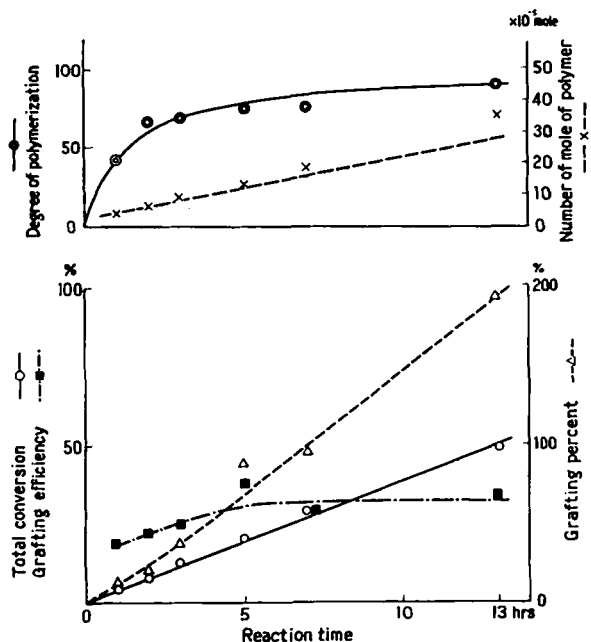


Fig. 4. Grafting of  $\beta$ PL purified by  $\text{CaCl}_2$ : (●) degree of polymerization; (×) number of moles of polymer; (○) total conversion; (■) grafting efficiency; (Δ) per cent grafting.  $[\text{DK}]_0/[\beta\text{PL}]_0$ , 1.37/100 (molar); trunk polymer, 100 mg. (DK, 9.1 mole-%);  $\beta$ PL 1 cc.;  $\text{CH}_3\text{ONa}$ ,  $1 \times 10^{-5}$  mole;  $60^\circ\text{C}$ .; *in vacuo*.

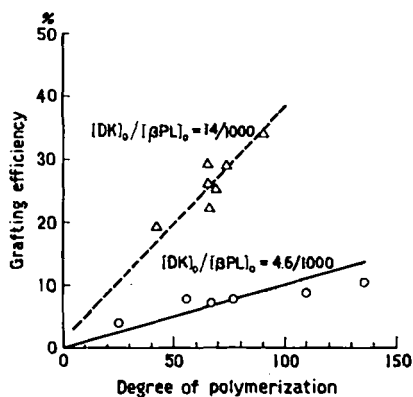


Fig. 5. Effect of degree of polymerization of  $\text{P}\beta\text{PL}$  on grafting efficiency.

of trunk polymer compared to Figure 2. On that occasion, the grafting efficiency was about three times greater than that in Figure 2 and increased as a function of molecular weight of  $\text{P}\beta\text{PL}$ .

A correlation between molecular weight of  $\text{P}\beta\text{PL}$  produced and grafting efficiency is shown in Figure 5.

### Effect of DK Content in Trunk Polymer

$\beta$ PL was grafted by sodium methylate catalyst onto PAN containing 1.0–22.5 mole-% DK (Fig. 6). The total conversion of P $\beta$ PL and molecular weight of homopolymer was independent of DK content. The per cent grafting and grafting efficiency increased with DK content in trunk polymer. In the case of the graft copolymerization of  $\beta$ PL onto pure PAN, the per cent grafting was about 6% for 5 hr. at 60°C., and therefore graft copolymerization by chain transfer to AN unit was negligible.

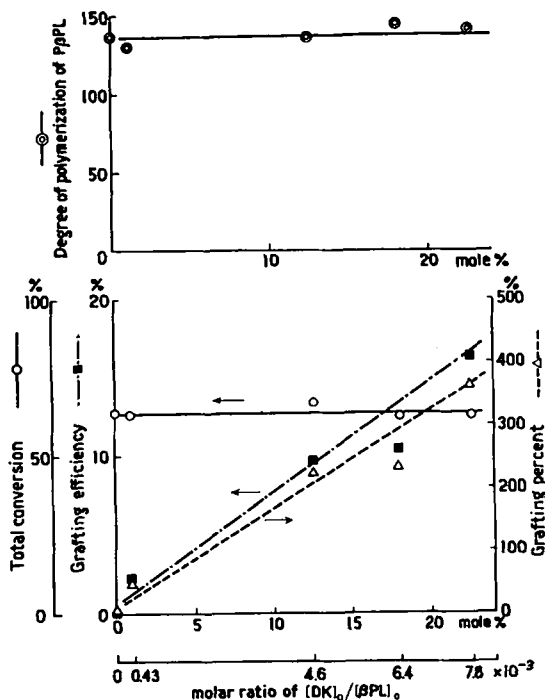


Fig. 6. Effect of DK content in trunk polymer on the grafting: (⊙) degree of polymerization of P $\beta$ PL; (○) total conversion; (■) grafting efficiency; (△) per cent grafting. Trunk polymer, 100 mg.;  $\beta$ PL, 3 cc.;  $\text{CH}_3\text{ONa}$ ,  $3.3 \times 10^{-3}$  mole; 60°C.; 5 hr.; *in vacuo*.

### Copolymer Composition for Copolymerization of Polymeric Lactone and $\beta$ PL

The copolymer composition curve is shown in Figure 7.

It is assumed that no crosslinks are formed in the graft copolymer, since the grafting efficiency was comparatively low.

Therefore, DK content in copolymer was calculated by assuming one DK unit per branch of P $\beta$ PL graft copolymerized.

Graft copolymerization was examined at only low concentration of DK (polymeric lactone) for reasons of the limited solubility of DK-AN co-







The absorption band ( $1810\text{ cm.}^{-1}$ ) of the lactone ring decreased and an absorption band ( $1670\text{ cm.}^{-1}$ ) assigned to sodium carboxylate appeared.

This trunk polymer including active points was thoroughly washed with absolute methanol, and  $\beta$ PL was added (Table I).

Grafting efficiency was higher as compared with the previous experiment (Fig. 2).

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

$\beta$ PL was polymerized by KOH in the presence of PMMA trunk polymer and then graft copolymer was produced effectively.

Graft copolymer was separated by Soxhlet extraction in toluene under reduced pressure.

The soluble fraction was unreacted trunk polymer which was determined by the infrared spectrum.

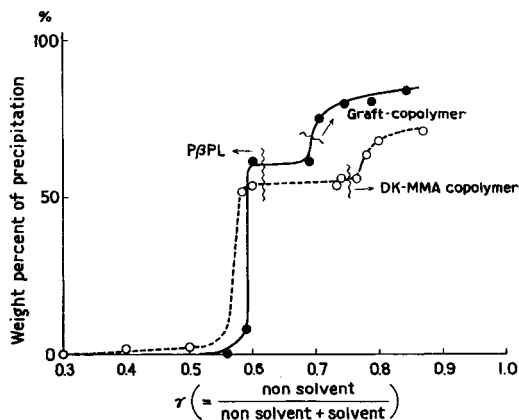


Fig. 9. Fractional precipitation of toluene-insoluble fraction in graft copolymer of  $\beta$ PL onto PMMA trunk polymer: (O) PMMA trunk polymer- $\beta$ PL mixture; (●) toluene-insoluble fraction of graft copolymer.

The insoluble fraction was fractionally precipitated by methanol from chloroform solution as shown in Figure 9, and was separated into graft copolymer and homopolymer.

$\beta$ PL polymerized in the absence of trunk polymer was precipitated completely in the range of  $\gamma = 0.33-0.60$  ( $\gamma$  is volume ratio of nonsolvent/nonsolvent + solvent), then trunk polymer began to be precipitated at  $\gamma = 0.76$ , and graft copolymer was precipitated at an intermediate fraction (Fig. 9). Results of graft copolymerization shown in Table II indicated that grafting efficiency was 35-60% and higher than in the case of DK-AN copolymer. The higher per cent grafting is attributed to chain transfer to MMA unit in the trunk polymer as described below.

TABLE II  
Graft Copolymerization of  $\beta$ PL onto PMMA Trunk Polymer\*

Expt. no.	KOH, mole/l.	Total conversion, %	Fractionation			Grafting, %	Graft-efficiency, %
			Trunk polymer, g.	Graft copolymer, g.	P $\beta$ PL, g.		
3	$2 \times 10^{-3}$	75	0.047	0.356	0.559	303	35
4	$4 \times 10^{-3}$	76	0.031	0.586	0.366	517	59
5	$5 \times 10^{-3}$	87	0.031	0.520	0.555	451	45

\* Trunk polymer, 100 mg.;  $\beta$ PL, 1 cc.; toluene, 8.8 cc.; DK content in trunk polymer, 7 mole-%; 60°C.; 148 hr.

### Chain Transfer Graft Copolymerization onto PMMA

For the graft copolymerization onto PMMA trunk polymer, active points such as  $-\text{COONa}$  may be produced on the trunk polymer by hydration of MMA units or chain transfer to MMA units, and then these active points will initiate graft copolymerization.

To investigate such chain transfer grafting,  $\beta$ PL was polymerized by potassium hydroxide in the presence of PMMA.

Graft copolymer was obtained as shown in Table III.

Per cent grafting onto DK-MMA copolymer (7 mole-% DK and 93 mole-% MMA) and PMMA were 303% (Table II, expt. 3) and 155% (Table III, expt. 6), under the same condition.

Therefore, in grafting onto DK-MMA copolymer, the amount of branch polymer grafted onto 7 mole-% DK units is almost the same as that grafted onto 93 mole-% of MMA units.

Then molar grafting activity of the DK unit is about 13 times that of MMA unit.

### Graft Copolymerization by Polymer Reaction Between P $\beta$ PL and DK-MMA Copolymer

Graft copolymerization by the reaction between P $\beta$ PL and DK-MMA copolymer was investigated (Table IV).

No graft copolymer was produced by the reaction in toluene which dissolved trunk polymer but not P $\beta$ PL.

On the reaction in chloroform which was a good solvent for both polymers, the formation of graft copolymer was confirmed.

### Graft Copolymerization by Cationic Catalyst

$\beta$ PL was polymerized by cationic catalysts such as stannic chloride, boron trifluoride-diethyl ether complex, or *p*-toluenesulfonic acid in the presence of trunk polymer containing DK units.

The results are shown in Table V.

TABLE III  
 Graft Copolymerization of  $\beta$ PPL onto PMMA<sup>a</sup>

Expt. no.	PMMA, g.	$\beta$ PPL, cc.	Toluene, cc.	KOH, mole/l.	Total Conversion, %	Fractionation			
						PMMA, g.	Graft polymer, g.	$\beta$ PPL, g.	Grafting efficiency, %
6	0.1	1.0	8.8	$2 \times 10^{-2}$	89	0.090	0.165	0.878	155
7	0.1	1.0	8.8	$10^{-2}$	81	0.091	0.238	0.714	230

<sup>a</sup> Reaction temp., 60°C.; reaction time, 148 hr.

TABLE IV  
Reaction Between PMMA Trunk Polymer and P $\beta$ PL

Expt. no.	Trunk polymer (PMMA), g.	P $\beta$ PL, g.	Potassium in P $\beta$ PL, mole/l.	Solvent	Fractionation				Grafting efficiency, %
					Trunk polymer, g.	Graft co-polymer, g.	P $\beta$ PL, g.	Grafting, %	
8	0.1	0.9	$2 \times 10^{-2}$	CHCl <sub>3</sub> (8.8 cc.)	0.082	0.290	0.470	272	3.8
9	0.1	0.9	$10^{-2}$	CHCl <sub>3</sub> (8.8 cc.)	0.088	0.470	0.231	458	6.7
10	0.1	0.9	$2 \times 10^{-3}$	Toluene (8.8 cc.) + $\gamma$ -butyrolactone (1 cc.)	0.091	Trace	0.855	$\sim 0$	—
11	0.1	0.9	$2 \times 10^{-3}$	Toluene (8.8 cc.) + $\gamma$ -butyrolactone (1 cc.)	0.096	$\sim 0$	0.885	$\sim 0$	—

TABLE V  
Graft Copolymerization of  $\beta$ PL onto PAN Trunk Polymer by Cationic Catalysts

Expt. no.	Trunk polymer (PAN), g.	$\beta$ PL, CC	Catalyst	Temp., °C.	Time, hr.	Total conversion, %	Grafting, %	Grafting efficiency, %	$\overline{DP}$ of homopolymer
12	0.1	1	$\text{BF}_3\text{OEt}_2$ ( $1.6 \times 10^{-3}$ mole/l.)	60	24	50	127	4.4	16
13	0.1	1	$\text{SnCl}_4$ ( $10^{-3}$ mole/l.)	40	5	15	15	2.9	21
14	0.1	1	"	60	5	25	19	2.2	18
15	0.1	1	"	70	5	8	35	13.2	19
16	0.1	3	$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ ( $10^{-3}$ mole/l.)	60	133	5	63	35.5	46

The rate of polymerization with cationic catalyst was lower than that with anionic catalyst.

In the grafting by *p*-toluenesulfonic acid, grafting efficiency was higher, but on grafting by stannic chloride or boron trifluoride-diethyl ether complex, the grafting efficiency was lower.

It has been pointed out by Yamashita<sup>3</sup> and Nakayama<sup>4</sup> that  $\beta$ -disubstituted  $\beta$ -propiolactone is difficult to polymerize by anionic catalyst but is polymerized easily by cationic catalyst.

The lower grafting efficiency in cationic grafting is attributed to lower degree of polymerization of P $\beta$ PL.

In case of cationic polymerization of  $\beta$ PL catalyzed by *p*-toluenesulfonic acid, the degree of polymerization of P $\beta$ PL produced is comparatively higher, and therefore grafting efficiency is high (expt. 16, Table V).

### Structure of Graft Copolymer

The infrared spectra of trunk polymer, graft copolymer, and homopolymer are shown in Figure 10.

In the infrared spectrum of PAN trunk polymer, absorptions characteristic of C $\equiv$ N (2200 cm.<sup>-1</sup>) and the lactone ring (1810 cm.<sup>-1</sup>) are observed (Fig. 10a).

When  $\beta$ PL was graft copolymerized by sodium methylate or stannic tetrachloride onto this trunk polymer, the absorption of lactone decreased and the absorption of ester carbonyl (1740 cm.<sup>-1</sup>) in branching P $\beta$ PL appeared (Fig. 10b,c).

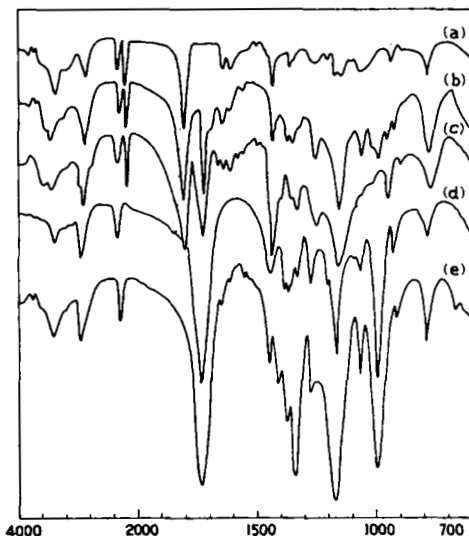


Fig. 10. Infrared spectra of: (a) trunk polymer (DK-AN copolymer); (b) graft copolymer obtained with CH<sub>3</sub>ONa catalyst; (c) graft copolymer obtained with SnCl<sub>4</sub> catalyst; (d)  $\beta$ PL homopolymer produced with CH<sub>3</sub>ONa catalyst; (e)  $\beta$ PL homopolymer produced with SnCl<sub>4</sub> catalyst.

The spectra of homopolymers byproduced in the graft copolymerization by sodium methylate and stannic chloride are of type I and type II,<sup>5-7</sup> respectively (Fig. 10*d,e*).

In the spectra of graft copolymers, those types of crystalline bands could not be detected because of the low per cent grafting. Such crystalline bands could be detected in the spectrum of trunk polymer- $P\beta$ PL mixture precipitated from DMF solution.

From these results, it seems that the short branching polymers on the graft copolymer could not be crystallized.

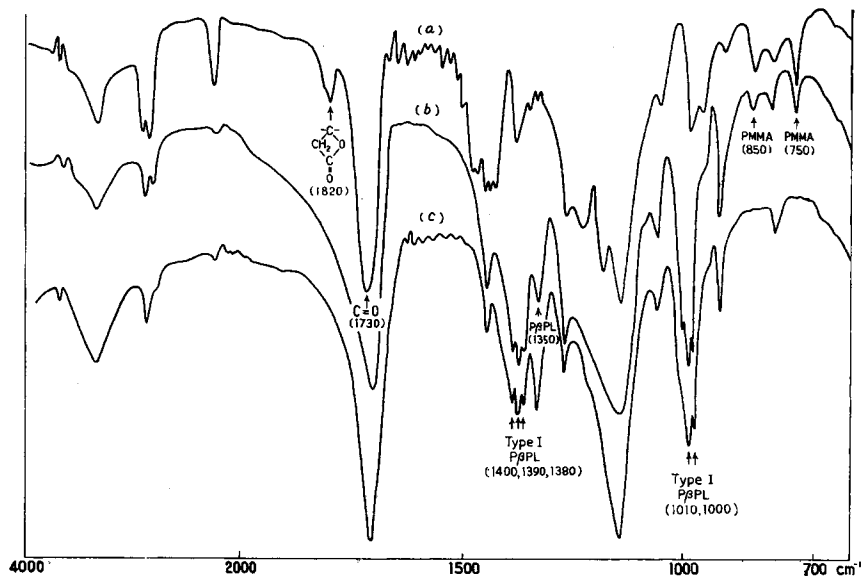


Fig. 11. Infrared spectra of: (a) trunk polymer (DK-MMA copolymer); (b) graft copolymer obtained with KOH catalyst; (c)  $\beta$ PL homopolymer.

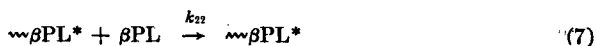
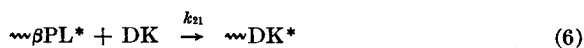
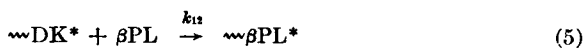
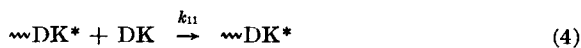
Spectra of graft copolymer onto trunk polymer (DK-MMA copolymer) are shown in Figure 11.

In this case, the crystalline bands of branching  $P\beta$ PL could be detected because of the higher per cent grafting, as shown in Figure 11*b*.

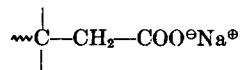
## DISCUSSION

### Copolymer Composition

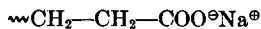
The reactions involved are shown in eqs. (4)–(7).



Propagating chain ends for both DK and  $\beta$ PL are primary sodium carboxylates, such as



or



Therefore, if a steric effect by trunk polymer is neglected, reactivity of these propagating chain ends may be similar.

$$k_{11} \stackrel{\cdot}{=} k_{21} \quad (8)$$

$$k_{12} \stackrel{\cdot}{=} k_{22}$$

The reactivity ratios  $r_1$  and  $r_2$  are

$$r_1 = k_{11}/k_{12} \quad (9)$$

$$r_2 = k_{22}/k_{21}$$

From eqs. (8) and (9),

$$r_1 r_2 = 1 \quad (10)$$

The monomer reactivity ratios  $r_1$  and  $r_2$  could not be determined accurately by common methods because of the restriction of low DK concentration, so they were determined by the comparison of experimental composition curves with the theoretical copolymer composition curves.

$r_1$  and  $r_2$  obtained were 0.3–0.1 and 3.6–9.1; respectively. Therefore, the reactivity ratio of DK/ $\beta$ PL was evaluated approximately to be 0.1–0.3.

### Relationship Between Grafting Efficiency and Degree of Polymerization of $\beta$ PL

If it is assuming that the length of branching  $\beta$ PL on graft copolymer is equal to the degree of polymerization for homopolymer and there is one DK unit in one branching  $\beta$ PL by copolymerization, then the grafting efficiency  $E$  is given by eq. (11):

$$E = ([\text{DK}]_p \bar{P} / [\beta\text{PL}]_p) \times 100 \quad (11)$$

where  $[\text{DK}]_p$  is moles of DK copolymerized,  $[\beta\text{PL}]_p$  is total moles of  $\beta$ PL polymerized, and  $\bar{P}$  is length of branching  $\beta$ PL.

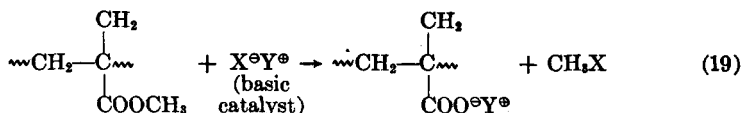
A higher degree of polymerization of  $\beta$ PL will favor higher grafting efficiency.

The expected correlation between degree of polymerization of  $\beta$ PL and grafting efficiency are confirmed in Figure 5.

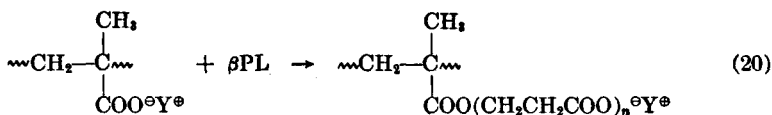




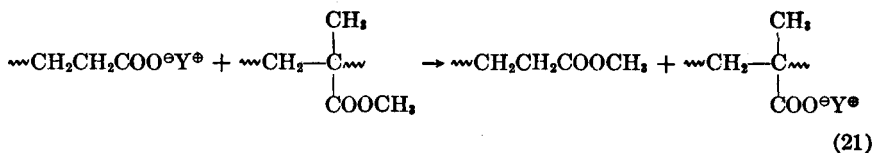
Initiation:



Propagation:



Chain Transfer:



When catalyst attacks  $\beta\text{PL}$ , homopolymer is produced by reactions shown in eqs. (13) and (15).

When the propagating chain end of homopolymer copolymerizes with DK in the trunk polymer, graft copolymer is obtained as shown in eq. (16).

Chain transfer of propagating homopolymer end to  $\beta\text{PL}$  or to impurity [eqs. (17), (18)] causes a decrease in the degree of polymerization of homopolymer, but does not affect graft copolymerization.

Chain transfer of propagating graft copolymer causes termination of graft copolymerization.

Graft copolymerization by chain transfer to AN units in the trunk polymer cannot be confirmed.

This method of graft copolymerization produces a large amount of homopolymer because reaction with  $\beta\text{PL}$  and catalyst predominates over reaction with DK in trunk polymer and catalyst. When DK-AN copolymer was treated with NaOH prior to the addition of  $\beta\text{PL}$  and active points were induced on the trunk polymer, the grafting efficiency was higher.

The graft copolymerization by polymer catalyst also was studied in another paper.<sup>1</sup>

Active sites will be also produced by hydrolysis of the MMA unit [eq. (19)] as well as by the initiation reactions [eqs. (12), (13)].

Initiation reactions [eqs. (12), (18)] are followed by propagation reactions [eqs. (14), (21)], and then graft copolymer will be produced.

When propagating homopolymer end undergoes chain transfer to MMA unit in trunk polymer [eq. (21)], an active point is produced on the trunk polymer, and graft copolymerization follows.

In conclusion, graft copolymer is produced by reactions (12), (14), (16), (19)–(21), and homopolymer is produced by reactions (13), (15), (17), and (18).

Higher grafting efficiency onto the PMMA trunk polymer is attributed to chain transfer of MMA unit in trunk polymer (Fig. 6, Table II).

### Cationic Graft Copolymerization of $\beta$ PL onto DK-AN Copolymer

Yamashita et al.<sup>3</sup> and Nakayama et al.<sup>4</sup> reported that  $\beta$ -disubstituted  $\beta$ -lactones polymerized with difficulty with alkali catalyst but polymerized easily with cationic catalyst.

In the cationic graft copolymerization, grafting efficiency was unexpectedly lower, because chain transfer occurs readily and a low molecular weight P $\beta$ PL is produced in cationic polymerization.

### CONCLUSION

$\beta$ PL was copolymerized by cationic or anionic catalyst with a polymeric lactone such as DK-AN copolymer or DK-MMA copolymer, and a graft copolymer was obtained.

A higher mole ratio of DK/ $\beta$ PL and a higher degree of polymerization of P $\beta$ PL favored higher grafting efficiency.

The reactivity ratio of polymeric lactone to  $\beta$ PL was about 0.1–0.3. In the graft copolymerization onto PAN trunk polymer, grafting by chain transfer to AN units in the trunk polymer was not detected, but in the grafting onto PMMA trunk polymer, there was grafting to MMA units.

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### Résumé

Un copolymère greffé de polyacrylonitrile- $\beta$ -propiolactone ( $\beta$ PL) a été synthétisé au moyen de la polymérisation ionique de la  $\beta$ PL en présence de polyacrylonitrile contenant des unités dicaténiques et en utilisant des catalyseurs basiques. Un copolymère greffé a été produit par polymérisation de  $\beta$ PL avec l'anneau lactonique dans la chaîne principale du polymère; dans cette méthode de copolymérisation greffée, l'efficacité de greffage est basse. Toutefois, l'efficacité de greffage croît avec le rapport molaire de lactone polymérique à  $\beta$ PL et un poids moléculaire plus élevé de P $\beta$ PL favorisait l'efficacité de

greffage plus élevée. Le rapport de réactivité de la lactone polymérique à  $\beta$ PL a été estimé être de l'ordre de 0.1 à 0.3.

### Zusammenfassung

Polyacrylnitril- $\beta$ -Propiolacton-( $\beta$ PL)-pfropfcopolymere wurden durch ionische Polymerisation von  $\beta$ PL mit basischen Katalysatoren in Gegenwart von Polyacrylnitril mit Diketenbausteinen in der Kette synthetisiert. Ein Pfropfcopolymeres wurde durch Copolymerisation von  $\beta$ PL mit dem Lactonring im Stammpolymeren erzeugt. Die Pfropfausbeute bei dieser Pfropfcopolymerisationsmethode war niedrig. Sie nahm aber mit steigendem Molverhältnis polymeres Lacton zu  $\beta$ PL zu und auch höheres Molekulargewicht von P $\beta$ PL begünstigte eine höhere Pfropfausbeute. Das Reaktivitätsverhältnis polymeres Lacton zu  $\beta$ PL liegt im Bereich von 0,1 ~ 0,3.

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