Ionic Graft Copolymerization.   II.   Graft Copolymerization of β-Propiolactone onto Acrylonitrile–Sodium Acrylate Copolymer
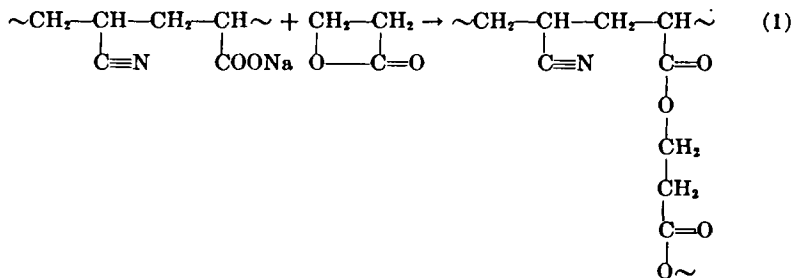
TETSUYA SHIOTA and YUTAKA GOTO, *Research Institute for Production Development, Kyoto, Japan*, and KOICHIRO HAYASHI, *Department of Polymer Chemistry, Kyoto University, Kyoto, Japan*

Synopsis

Polyacrylonitrile–β-propiolactone (βPL) graft copolymer was synthesized by means of ionic polymerization, in which polymerization of βPL was initiated by polyacrylonitrile containing a small amount of some reactive groups such as —COOK, —COONa, —COOLi, and —COOH.   Lower electronegativity of the countercation favored higher total conversion and higher grafting percentage.   The grafting percentage increased with the reaction time and concentration of reactive groups in the trunk polymer, but grafting efficiency varied very little under these conditions.   In the bulk polymerization at 60°C., grafting efficiency was about 60%, but in the solution polymerization in toluene or dioxane, grafting efficiency was higher than in bulk or nitrobenzene.

INTRODUCTION

β-Propiolactone (βPL) has been polymerized easily by various kinds of catalysts.[1-5]   Daul et al. have reported graft polymerization of βPL onto cellulose fiber,[6-9] Rose et al.,[10] and Fearnley and Speakman[11] have reported graft copolymerization onto wool.   Gresham[1] pointed out that PβPL formed by sodium acetate polymerization contained an acetyl group on one end of the polymer and a carboxyl group on the other end.   By analogy to these results, graft copolymer must be produced by the polymerization of βPL initiated by a polymeric catalyst such as polyacrylonitrile (PAN) containing some alkali metal carboxylate.   βPL was graft copolymerized onto acrylonitrile–alkali metal acrylate copolymer (AN–AK, AN–ANa, or AN–ALi copolymer).

$$\sim CH_2—CH—CH_2—CH\sim + CH_2—CH_2 \rightarrow \sim CH_2—CH—CH_2—CH\sim \qquad (1)$$

Our previous paper[12] reported the synthesis of PAN-βPL graft copolymers by means of ionic polymerization in which βPL was copolymerized with lactone groups in diketene (DK)–AN copolymer by basic catalysts.

$$\sim CH_2-CH-CH_2-C-\ \ \ +\ CH_2-CH_2$$

$$\xrightarrow[CH_3ONa]{} \sim CH_2-CH-CH_2-C\sim \qquad (2)$$

In this latter method, the grafting efficiency is very low because of the lower reactivity of the DK unit in the trunk polymer. But in the former method, βPL is graft copolymerized with higher grafting efficiency. The investigation of the polymerization of βPL catalyzed by sodium acetate has been reported in another paper,[13] in which the behavior was compared with the results of this graft copolymerization.

EXPERIMENTAL

Reagents

Trunk Polymer. AN–acrylic acid (AA) copolymer in powder form (80–100 mesh) containing 23 mole-% AA unit, was reacted with alkali metal hydroxide in methanol solution and was washed with absolute methanol.

This trunk polymer contains 1.8 mole-% (3.1×10^{-5} mole/0.1 g. trunk polymer) sodium acrylate units, was determined by gravimetric analysis by the zinc uranyl acetate method.[14,15]

βPL. βPL was purified by calcium chloride as shown in the previous paper.[16]

Toluene, Dioxane, and Nitrobenzene. These solvents were purified by the usual procedure.

Procedure of Graft Copolymerization

In the bulk graft copolymerization, 3 cc. of βPL was added to 100 mg. of dried trunk polymer in a dry box, and the reaction tube was evacuated

by using a high-vacuum technique ($<10^{-4}$ mm. Hg). In the solution graft copolymerization, 100 mg. of trunk polymer, 9 cc. of solvent, and 1 cc. of βPL were added into a reaction tube by the same procedure.

Separation of Graft Copolymer

The crude product was extracted with 20 times its volume of chloroform at 60°C. for 3 hr., followed by adding methanol (0.8 times volume of chloroform), and the graft copolymer was separated. The mixture of PβPL and trunk polymers was separated perfectly by this method. The per cent grafting was determined from the weight gain of graft polymer.

Determination of Molecular Weight for PβPL

Molecular weight of PβPL was determined by the same viscometric method as described in a previous paper.[13]

Determination of Endgroups of PβPL

Carboxyl group and double bond contents were determined by the same method given on our previous paper.[13]

RESULTS

Effect of Reaction Time on the Bulk Graft Copolymerization

βPL purified by CaCl$_2$ was grafted onto AN–ANa copolymer containing 1.8 mole-% ANa in bulk at 60 and 30°C. (Figs. 1 and 2). Total conversion and per cent grafting increased with reaction time, but grafting efficiency was estimated to be ca. 60%, regardless of the reaction time. This result indicates that chain transfer occurs frequently in the early period of graft copolymerization and thereafter that occurs only rarely, in the same manner as in homopolymerization,[13] in which the ratio of polymer and catalyst increased in the earlier period and thereafter that varied only very slightly. The frequent chain transfer in the earlier period of polymerization is also supported by the results in which the number of homopolymer molecules produced as a by-product in graft copolymerization is almost equal to number of double bonds in the homopolymer, and mole ratio of double bonds per PβPL produced in homopolymerization by sodium acetate is estimated to be about 0.5. The rate of graft copolymerization is larger than that of homopolymerization (compare Fig. 1 of this paper with Fig. 2 of our previous paper[13]); this result may be attributable to differences in acidity of anions and solubility of catalyst. That is, AN–ANa copolymer is a secondary carboxylate and easily soluble in monomer, but sodium acetate is a primary carboxylate and slightly soluble. The branching length of the graft copolymer is longer than the degree of polymerization of homopolymer, and this is similar to a gelation effect in radical graft copolymerization; however in the ionic polymerization such a gelation effect would hardly be expected. It is therefore supposed that this result may
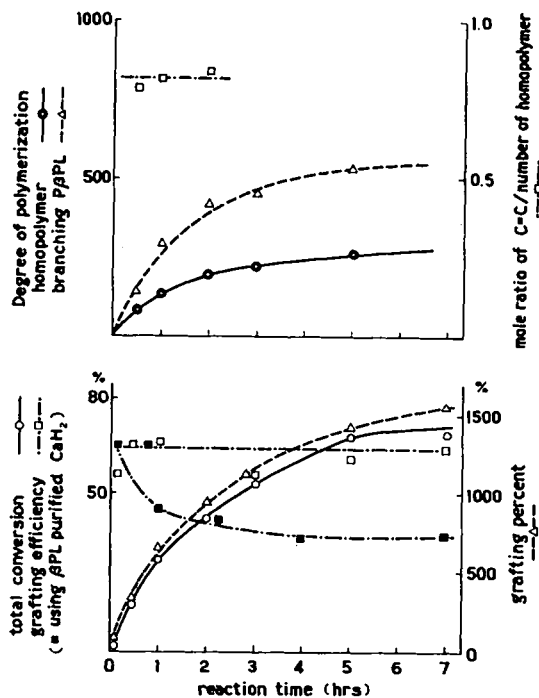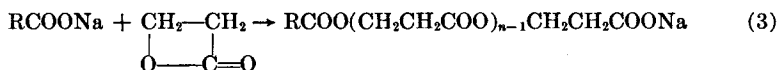
Fig. 1. Grafting of βPL onto AN–ANa copolymer in bulk at 60°C.: (○) degree of polymerization of homopolymer; ($\triangle$) degree of polymerization of branching PβPL; (□) mole ratio of C=C/homopolymer; (Ⓞ) total conversion; (□) grafting efficiency; (■) grafting efficiency with βPL dried with CaH$_2$; ($\triangle$) per cent grafting. Trunk polymer, 100 mg., Na in trunk polymer 3.1×10^{-4} mole; βPL, 3 cc.; 60°C.

be attributed to the effect of neighboring groups such as CN in the trunk polymer. As shown in our previous paper,[16] βPL purified by CaH$_2$ contained some amount of water (H$_2$O > 300 ppm) and a chain transfer reaction occurred frequently, but in the case of βPL purified by CaCl$_2$ (H$_2$O < 10 ppm), chain transfer reaction occurred only to a small extent. When βPL purified with CaH$_2$ was used in the graft copolymerization, the grafting efficiency decreased with reaction time, as shown in Figure 1. This shows that chain transfer occurs more easily in the case of βPL purified by CaH$_2$.

Homopolymerization of βPL with Sodium Hydroxide, Sodium Isobutylate, Sodium Acetate, or Sodium Acrylate as Catalyst

The behavior of homopolymerizations catalyzed by NaOH, (CH$_3$)$_2$-CHCOONa, CH$_3$COONa, or CH$_2$=CHCOONa can be compared with graft copolymerization (Table I). These catalysts have the same cation and different anions. Polymerization activity is affected by the acidity of anion. The rate of polymerization increases in the order: NaOH > (CH$_3$)$_2$-CHCOONa > CH$_3$COONa > CH$_2$ = CHCOONa, which coincides with the order of pK_a of the anions.

$$RCOONa + \underset{\substack{| \quad | \\ O \underline{\quad} C = O}}{CH_2 \underline{\quad} CH_2} \rightarrow RCOO(CH_2CH_2COO)_{n-1}CH_2CH_2COONa \qquad (3)$$

In the polymerization of βPL initiated by alkali catalysts, the growing chain end of PβPL is a primary carboxyl group which is foreign to the anion from the catalyst. Therefore the nature of the anion in the catalyst should influence the polymerization behavior only in the initiation step. These arguments cannot explain the effect of the catalyst anion, because the polymerization of βPL proceeds step by step and the rate-determining step is the propagation reaction. A higher pK_a of the catalyst anion favors higher polymerization activity, which favors a higher efficiency of initiation because of the following physical factor. These catalysts are only slightly soluble in monomer but PβPL is quite soluble. Therefore these catalysts dissolve gradually in monomer as a result of the reaction with βPL. The higher the pK_a of anion, that is, the higher the electron density of the anion, the more easily the β-carbon of βPL is attacked in the reaction of catalyst with βPL, and therefore the higher the efficiency of initiator is. On the other hand, the nature of the anion in the catalyst may influence the rate of propagation, because the counter cation exists in a complex form associated with catalyst because of the relative insolubility of the catalyst and also because of anion effects on electronegativity of the counter cation.[2] The rate of polymerization for total conversion in graft copolymerization is close to that of sodium isobutylate.
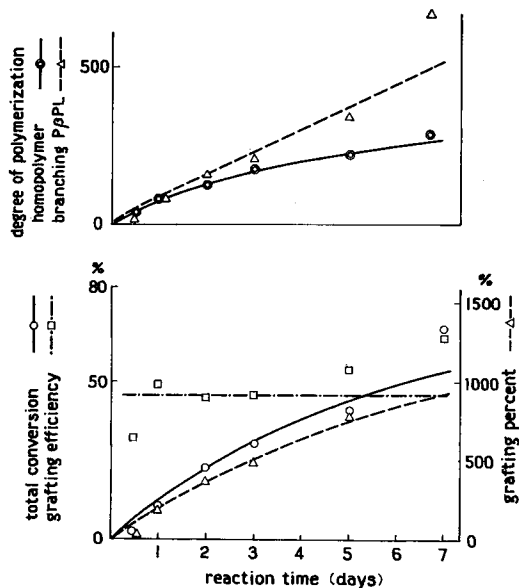

Fig. 2. Grafting of βPL onto AN–ANa copolymer in bulk 30°C.; (●) degree of polymerization of homopolymer; (△) degree of polymerization of branching PβPL; (○) total conversion; (□) grafting efficiency; (△) per cent grafting. Trunk polymer, 100 mg.; Na in trunk polymer, 3.1×10^{-5} mole; βPL, 3 cc.; 30°C.

TABLE I
Polymerization of βPL by NaOH, Sodium Isobutylate, Sodium Acetate, or Sodium Acrylate[a]

Catalyst	Rate of polymerization, %/hr.	Degree of polymerization	Mole ratio of C=C/ PβPL	pK$_a$ of acid
Polymerization of βPL				
NaOH	38	165	0.6	14.0
CH$_3$ CH—COONa CH$_3$	28	133	0.6	4.84
CH$_3$COONa	26	153	0.4	4.76
CH$_2$=CH COONa	12	109	0.8	4.25
Graft copolymerization				
Total reaction	—	30	155	0.5	—
Homopolymerization	—	19	105	0.7	—

[a] βPL, 9 cc.; catalyst, 9.3 × 10^{-3} mole; 60°C.; 45 min.

Effect of Reaction Temperature

βPL was grafted onto AN–ANa copolymer in bulk at various temperatures (Table II). Total conversion and per cent grafting increased with increasing reaction temperature. Arrhenius plots of the rate of poly-

TABLE II
Effect of Temperature on the Grafting of βPL onto AN–ANa Copolymer in Bulk[a]

Reaction temperature, °C.	Reaction time, hr.	Total conversion, %	Grafting, %	Grafting efficiency %	Average, %
60	1	29	658	66	
	3	53	1015	55	62
	7	69	1535	64	
50	1	10	90	39	
	3	21	275	44	45
	7	35	572	52	
40	1	3	51	53	
	7	15	308	60	57
30	7	2	25	32	
	24	11	180	49	42
	48	23	348	45	

[a] Trunk polymer, 100 mg.; Na in trunk polymer, 3.1 × 10^{-5} mole; βPL, 3 cc.

merization for the total yield, grafting yield, or homopolymer yield are shown in Figure 3. The activation energies are 24.6 kcal./mole for total yield, 27.5 kcal./mole for grafting yield, and 23.6 kcal./mole for homopolymer yield. On the other hand, the activation energy for homo-
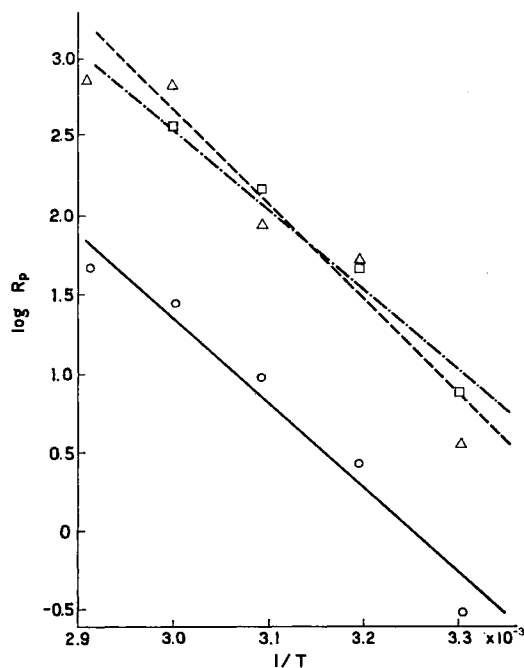
Fig. 3. Arrhenius plot for the graft copolymerization: (O) total conversion (E_a = 24.6 kcal./mole); (△) conversion of branching PβPL (E_a = 27.5 kcal./ mole); (□) conversion of homopolymer (E_a = 23.6 kcal./mole).

polymerization of βPL catalyzed by CH_3COONa is 23 kcal./mole, as shown in our previous paper,[13] which coincides almost exactly with that of graft copolymerization. The activation energy for the grafting yield is comparatively higher than the others, because it is apparently difficult for monomer to approach the growing end of the branching polymer for the reason of higher microviscosity.

Effect of Sodium Content in the Trunk Polymer

The effect of catalyst concentration on the graft copolymerization at fixed reaction time is shown in Figure 4. Total conversion and per cent grafting increase with sodium content in the trunk polymer, but grafting efficiency does not change. The degrees of polymerization of homopolymer and branching PβPL increase with lower catalyst concentration, and that of branching PβPL is higher than that of homopolymer.

Effect of Solvent

βPL was grafted onto AN–ANa copolymer in solvents having different dielectric constants: i.e., toluene, dioxane, and nitrobenzene (Figs. 5–7 and Table III). The trunk polymer is insoluble in these solvents, and PβPL is insoluble in toluene, partially soluble in dioxane, and soluble in nitrobenzene. The order of rate of grafting is toluene > nitrobenzene

> dioxane; this is the same order as for the CH₃COONa-catalyzed homopolymerization in the period after induction, and does not coincide with the order of dielectric constants. One reason for the higher rate of graft copolymerization in toluene is precipitation of the propagating
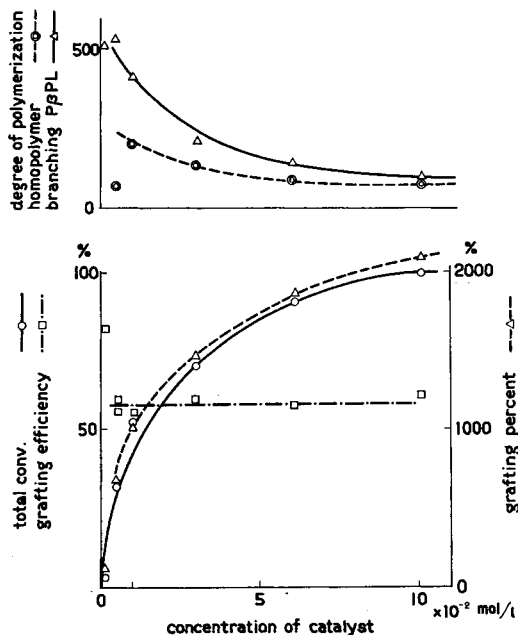
AN-ANa copolymer 100 mg, βPL 3 cc, 60°C, 3 hrs.

Fig. 4. Effect of Na content in trunk polymer: (●) degree of polymerization of homopolymer; (△) degree of polymerization of branching PβPL; (○) total conversion; (□) grafting efficiency; (▲) per cent grafting. AN–ANa copolymer, 100 mg.; βPL, 3 cc.; 60°C.; 3 hr.
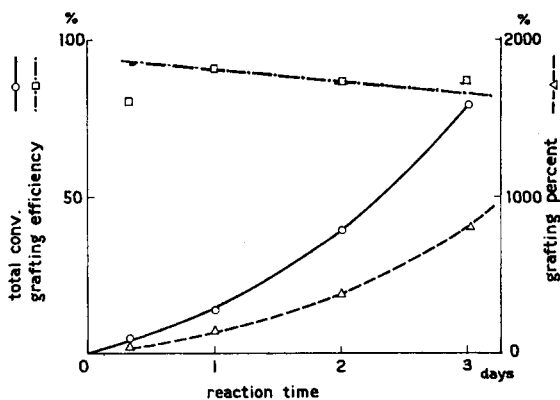

Fig. 5. Grafting of βPL onto AN–ANa copolymer in toluene solution: (○) total conversion; (□) grafting efficiency; (△) per cent grafting. Trunk polymer, 100 mg.; βPL, 1 cc.; toluene, 9 cc.; 60°C.
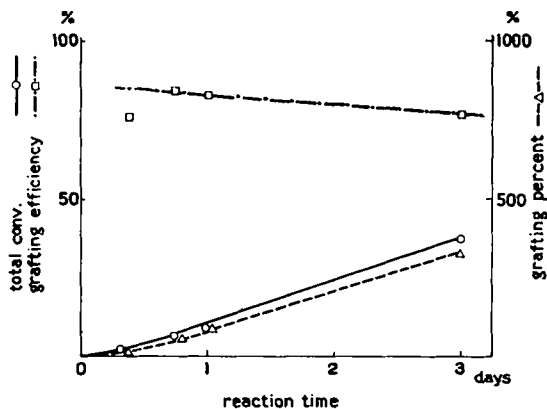
Fig. 6. Grafting of βPL onto AN–ANa copolymer in dioxane: (O) total conversion; (□) grafting efficiency; (△) per cent grafting. Trunk polymer, 100 mg.; βPL, 1 cc.; dioxane, 9 cc.; 60°C.
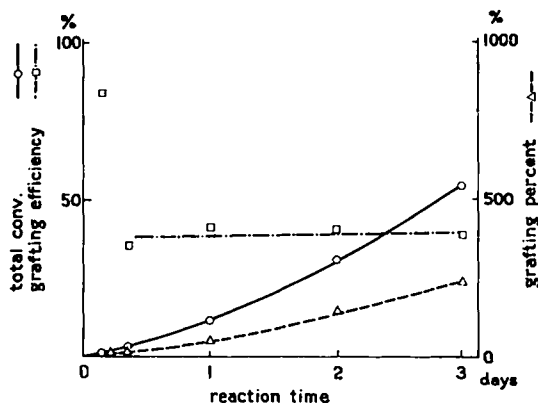

Fig. 7. Grafting of βPL onto AN–ANa copolymer in nitrobenzene; (O) total conversion; (□) grafting efficiency; (△) per cent grafting. Trunk polymer, 100 mg.; βPL, 1 cc.; nitrobenzene, 9 cc.; 60°C.

TABLE III
Effect of Solvent on the Graft Copolymerization

	In bulk	In solution		
		Nitrobenzene	Dioxane	Toluene
Reaction time, hr.	7	72	72	72
Total conversion, %	69	54	37	80
Grafting, %	1535	238	329	802
Grafting efficiency, %	64	38	77	87
Dielectric constant	42	34.3	2.23	2.38
Solubility of PβPL produced	1	2	3	4

active species.   In the graft copolymerization in a nonpolar solvent such as toluene or dioxane, grafting efficiency is very high.   In the homopolymerization,[13] the molar ratio of PβPL to catalyst is about 1 in toluene solution polymerization and about 2–3 in bulk or nitrobenzene.   These results demonstrate that chain transfer reaction occurs only to a very small extent in nonpolar solvent but easily in, polar solvent.

Effect of Catalyst Cation

βPL was grafted by the polymer catalysts having various cations, i.e., K+, Na+, Li+, H+, Ba++, and Ca++.   Total conversion and grafting per cent increase in the order: K+> Na+> Li+> H+; Ba++> Ca++, which is the same order as for homopolymerization[13,16] catalyzed by alkali metal acetate and is in reverse order to the electronegativity of cations (Table IV).

TABLE IV
Effect of Cations in Catalyst on Graft Copolymerization[a]

Catalyst		Reaction time, hr.	Total conversion, %	Grafting, %	Grafting efficiency, %	Electro-negativity cation
Anion	Cation					
—COO⁻	K+	7	~100	2740	79	0.8
"	Na+	0.5	14	316	64	0.9
"	"	7	69	1535	64	"
"	Li+	7	10	239	68	1.0
"	H+	7	4	96	66	2.1
"	"	24	17	240	42	"
"	Ba++	7	14	391	78	0.9
"	"	24	35	601	49	"
"	Ca++	2	2	82	100	1.0
"	"	13	13	236	53	"

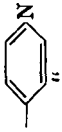[a] Trunk polymer, 100 mg.; catalyst, 3.1×10^{-5} mole; βPL, 3 cc.; 60°C.

The lower electronegativity of counter cation may contribute to dissociation of the ion pair.   Higashimura et al.[2] have reported that the rate of polymerization of βPL by alkali metal hydroxides and carbonates as catalyst is in the order of Cs+ > Rb+ > K+ > Na+, which coincides with our result.

Graft Copolymerization of βPL onto Various Polymer Catalysts

βPL was graft copolymerized with various polymer catalysts such as AN–4-vinylpyridine (AN–4VP) copolymer, sulfonated styrene–divinyl-benzene (St–DVB) copolymer, and AN–acrylic acid (AN–AA) copolymer (Table V).

In the graft copolymerization onto AN–AA copolymer, it would seem that βPL would be polymerized by protons in the cationic mechanism, and, if so, graft copolymer would not be accompanied by chain transfer of growing chain onto trunk polymer.   Nevertheless, βPL graft copolymerized on to AN–AA copolymer effectively.   This result may demonstrate that βPL

TABLE V

Graft Copolymerization of βPL onto Various Kinds of Polymer Catalyst[a,b]

Trunk polymer	Active group(s)	Solvent	Reaction time, hr.	Total conversion, %	Grafting, %	Grafting efficiency, %
AN–ANa copolymer	—COO Na	Toluene (90%)	7	4	36	81
"	"	"	24	13	138	90
"	"	Bulk	48	40	400	87
AN–AA copolymer	—COO H	Bulk "	7	69	1545	64
Na salt of sulfonated PSt	—SO₃ Na	Toluene	7	4	96	66
"	"	"	192	0.2	—	—
Sulfonated PSt	—SO₃ H	"	312	77	77	9
"	"	"	24	60	40	6
DVB–St–4VP copolymer	N (pyridyl ring)	"	48	76	111	3
"	"	"	24	85	253	26
"	"	"	48	92	394	37

[a] Solution polymerization: trunk polymer, 100 mg.; βPL, 1 cc.; toluene, 9 cc.; 60°C.
[b] Bulk polymerization: trunk polymer, 100 mg.; βPL, 3 cc.; 60°C.

polymerizes through the carboxyl anion of the carboxylic acid in an anionic mechanism. In the graft copolymerization onto sulfonated St–DVB copolymer, grafting efficiency is very small. This is probably caused by cationic polymerization initiated by the proton from the strong acid. In the case of AN–4VP copolymer, the grafting efficiency is very small. On the sodium sulfonated St–DVB copolymer, the rate of graft copolymerization and the grafting efficiency are both very low.

Structure of Polymer

In the infrared spectrum of trunk polymer (AN–AA copolymer), bands at 2200 (C≡N), 1740 (—C=O), and 1580 cm.$^{-1}$ (O $=$ C $=$ O$^{\ominus}$) are observed. When βPL was graft copolymerized onto that trunk polymer, the bands at 1740 cm.$^{-1}$ (corresponding to the ester carbonyl group), and in the neighborhood of 1400 and 1000 cm.$^{-1}$ (corresponding to polymer configuration) appeared. Absorption ratio of $D_{C=O}$ (1740)$/D_{C≡N}$ (2200) in the infrared spectrum of graft copolymer increases with increasing per cent grafting.

The key bands (in the neighborhood of 1400 and 1000 cm.$^{-1}$) assigned to the polymer configuration can not be observed on graft copolymer of low per cent grafting, but can be observed in the more highly grafted polymer. In other words, the shorter branching PβPL on the graft copolymer can not crystallize owing to the disturbance of trunk polymer, but the longer branch can crystallize. The infrared spectrum of branching PβPL shows a type II configuration, but that of the homopolymer by-product shows type I for lower molecular weight polymer and type II for higher molecular weight (Table VI).

The infrared spectrum of PβPL polymerized by alkali catalysts such as CH$_3$COONa, CH$_2$C=HCOONa, or NaOH shows also a type I spectrum for lower molecular weight material and a type II spectrum for higher molecular weight polymer.

In previous papers[2,16,17] it has been reported that the infrared spectrum of PβPL polymerized by alkali catalyst is type I and that of PβPL obtained with acid catalyst is type II. This is attributed to the difference in degree of polymerization, as described in detail in a previous paper.[13]

DISCUSSION

Lower Grafting Efficiency in Bulk Graft Copolymerization

If graft copolymerization of βPL proceeds by the mechanism as shown in eq. (1), grafting efficiency should be expected to be nearly 100%. In spite of careful operations, grafting efficiency was limited to 60% in the bulk graft copolymerization. To explain this unexpected lower grafting efficiency, it is necessary to consider several factors: (a) thermal or impurity initiation; (b) polymerization by protons from carboxyl groups remaining in trunk polymer which have escaped Na treatment; (c) polymerization

TABLE VI

Infrared Spectrum of PβPL or Graft Polymer

Time, hr.	Homopolymerization						Grafting			
	CH₃COONa		CH₂=CHCOONa		NaOH		Homo-polymer		Graft polymerization	
	Spectrum type	$[\eta]$	Spectrum type	$[\eta]$	Spectrum type	$[\eta]$	Spectrum type	$[\eta]$	Spectrum type	Grafting, %
0.5	I	0.13	I < II	0.16	II	0.24	I	0.17	Amorphous	316
1	I > II	0.18	II	0.26	II	0.33	I	0.24	II	944
2	II	0.25	—		—		I	0.31		
3	II	0.30	—		—		I	0.34		
7	II	0.37	—		—		I	0.17		

induced by some compounds formed on desiccating trunk polymer at 98°C.; (*d*) polymerization by free sodium hydroxide not washed off in preparation of trunk polymer (trunk polymer was treated with sodium hydroxide solution and washed by absolute methanol); (*e*) depolymerization of branching PβPL; (*f*) chain transfer to monomer.

These possible factors were investigated. First, purified βPL without catalyst was allowed to stand at 60°C. for 7 hr. *in vacuo*, but no polymer was produced; therefore initiation by heat or impurities is not the cause of the formation of homopolymer. To determine the possible effect of initiation by carboxyl protons, βPL was polymerized in the presence of AN–AA copolymer without sodium carboxyl groups at 60°C. for 7 hr. *in vacuo;* total conversion was negligibly small (about 4%) (Table V) in comparison with AN–ANa copolymer (Fig. 1). To determine the effect of compounds formed in drying the trunk copolymer, graft copolymerization onto trunk polymers dried under various conditions was carried out (Table VII), but grafting efficiency did not vary.

TABLE VII
Graft Copolymerization of βPL onto AN–ANa Copolymer
Dried under Various Conditions

| Expt. no. | Condition of drying trunk polymer[a] | | Total conversion, % | Grafting, % | Grafting efficiency, % |
	Temperature, °C.	Time, hr.			
1	130–140	3	27.0	534	57
2	98	1	26.9	588	63
3	"	3	27.3	606	64
4	"	5	25.3	523	60
5	"	8	27.1	595	63
6	60	3	27.5	610	64
7	20	24	24.6	560	65

[a] Dried by vacuum line; trunk polymer, 100 mg.; βPL, 3 cc.; 60°C., 1 hr.

TABLE VIII
Depolymerization of Branching PβPL on the Graft Copolymer

| Reaction time, hr. | Reprecipitated polymer[a] | | Graft copolymer after treatment | | Homopolymer wt., g. | Grafting efficiency, % |
	Wt., g.	%	Wt., g.	Grafting, %		
0	—	—	0.4000	321	0	100
1	0.3921	98.0	0.3879	308	0.0121	96.2
7	0.3953	98.9	0.3805	301	0.0195	93.7

[a] Mixture of graft copolymer and β-propiolactone homopolymer depolymerized graft copolymer before treatment, 0.4000 g.; γ-butyrolactone, 3.0 cc.; CH_3COONa, 3.1×10^{-5} mole; 60°C.

Therefore, it seems that trunk polymer did not decompose during the drying process. When graft copolymerization onto the same trunk polymer as that used in bulk was carried out in toluene solution (Fig. 5), the per cent grafting was very high, about 90%. This result denies the existence of unwashed sodium hydroxide on the trunk polymer. Depolymerization was studied by treating a graft copolymer solution in γ-butyrolactone with sodium acetate under the same conditions as graft copolymerization in bulk (Table VIII), but the decrease of per cent grafting was very small.

These investigations indicate that factors (a)–(e) are negative for the formation of homopolymer, and therefore chain transfer to monomer is most important.

Chain Transfer Reaction

Graft copolymerization is a convenient method for the elucidation of the chain transfer mechanism. In this graft copolymerization, the probability of the following three chain transfers can be supposed: (a) chain transfer to trunk polymer; (b) chain transfer to trace of impurity in monomer; (c) chain transfer to monomer.
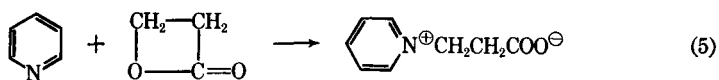
When βPL was allowed to stand in the presence of PAN under the same conditions as graft copolymerization, no graft copolymer was obtained. Therefore chain transfer onto PAN does not occur. The polymer from βPL purified by calcium chloride has a much higher molecular weight than that of conventionally purified βPL, as shown in our previous paper.[13,16] Also, in the graft copolymerization, the grafting efficiency obtained with βPL purified by calcium chloride is higher than that of conventionally purified βPL (Fig. 1). These results demonstrate that chain transfer reaction to impurity in monomer occurs frequently in the case of conventionally purified βPL. βPL was purified more strictly as follows: βPL purified by calcium chloride was polymerized by sodium acetate up to about 30% conversion and then the residual βPL was distilled under reduced pressure. This purified βPL was then graft copolymerized onto AN–ANa copolymer, but chain transfer reaction could not be prevented. Therefore chain transfer to monomer cannot be denied. In the bulk graft copolymerization, grafting efficiency was estimated to be about 60%, regardless of the reaction time (Fig. 1). This result indicates that chain transfer reaction occurs frequently in the earlier period of graft copolymerization and rarely in the later period. The same behavior of chain transfer was observed also in the homopolymerization.[13,16] Such chain transfer reaction does not occur to a large extent in a nonpolar solvent such as toluene or dioxane (Figs. 5 and 6), but occurs easily in a polar solvent such as nitrobenzene (Fig. 7).

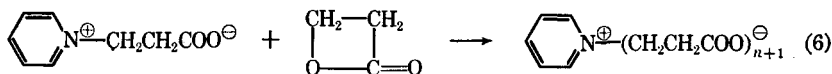### Graft Copolymerization of βPL by Various Polymeric Catalysts

Kagiya et al.[18] and Gresham[1] have reported that the polymerization of βPL occurs with pyridine catalyst and with inorganic acid, organic acid, and

their salts. In the present investigation, graft copolymerization of βPL was carried out with the use of various polymeric catalysts, such as AN–alkali metal acrylate copolymers, AN–AA copolymer, sulfonated St–DVB copolymer, sodium sulfonated DVB–St copolymer, and AN–4VP copolymer. The rate of graft copolymerization by polymeric catalysts containing alkali carboxyl groups, pyridine group (anionic catalyst), and the sulfonic acid group (cationic catalyst) is large, but that by catalyst containing a carboxyl group and a sodium sulfonyl group is very small. The order of nucleophilic nature of these anions is $-COO^{\ominus} > -SO^{\ominus}_3$, and the order of electrophilic nature of these cations is $Na^{\oplus} < H^{\oplus}$. Sodium carboxylate, which has the less electrophilic cation and the more nucleophilic anion will initiate the polymerization of βPL by an anionic mechanism, and sulfonic acid, consisting of the more electrophilic cation and the less nucleophilic anion will initiate the polymerization by a cationic mechanism. The comparatively higher grafting efficiency in the graft copolymerization by polymeric catalyst containing a sodium carboxylate group is caused by anionic initiation, and the much lower grafting efficiency in the grafting by polymeric catalyst containing the sulfonic acid group is caused by cationic initiation. It is of interest whether carboxylic acid with the more electrophilic cation and the more nucleophilic anion, and sodium sulfonate, with the less electrophilic cation and the less nucleophilic anion, can initiate polymerization of βPL in cationic or anionic mechanism. The comparatively higher grafting efficiency in the grafting on to AN–AA copolymer might support anionic graft copolymerization by carboxyl anion. On the other hand, the low grafting efficiency in the grafting onto sodium sulfonated St–DVB copolymer would not be caused by the anionic mechanism so much as by the cationic mechanism. Polymerization of βPL by catalysts such as pyridine[18] and betain[19] have been reported and the polymerization mechanisms of eqs. (5)–(7) have been proposed.
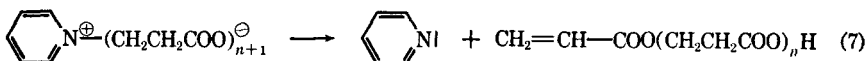
Initiation:

$$\text{pyridine} + \begin{array}{c} CH_2—CH_2 \\ | \quad\quad | \\ O——C{=}O \end{array} \longrightarrow \text{py}N^{\oplus}CH_2CH_2COO^{\ominus} \qquad (5)$$

Propagation.

$$\text{py}N^{\oplus}—CH_2CH_2COO^{\ominus} + \begin{array}{c} CH_2—CH_2 \\ | \quad\quad | \\ O——C{=}O \end{array} \longrightarrow \text{py}N^{\oplus}{-}(CH_2CH_2COO)^{\ominus}_{n+1} \qquad (6)$$

Termination:

$$\text{py}N^{\oplus}{-}(CH_2CH_2COO)^{\ominus}_{n+1} \longrightarrow \text{py}NI + CH_2{=}CH—COO(CH_2CH_2COO)_n H \qquad (7)$$

In the graft copolymerization onto AN–4VP copolymer, the grafting efficiency was very low, and these results support their assertion.

CONCLUSION

Graft copolymerization of βPL onto PAN was carried out by the method of anionic polymerization by polymeric catalysts containing alkali metal acrylate. This graft copolymerization proceeds with higher grafting efficiency than that of graft copolymerization by the methods of anionic copolymerization[12] between βPL and polymeric lactone, such as diketene–AN copolymer. In the bulk graft copolymerization onto AN–ANa copolymer, the grafting efficiency was estimated to be about 60% and independent of reaction time. This result indicates that chain transfer occurs frequently in the earlier period of graft copolymerization and only rarely in the later period; this parallels the results for of homopolymerization by sodium acetate catalyst. In the grafting in toluene solution, the rate of graft copolymerization was slower but grafting efficiency was very high, (about 90%), and little chain transfer occurred. However, in the grafting in dioxane, which has a higher dielectric constant, the grafting efficiency was as low as in the bulk. Countercations affect the rate of graft copolymerization but not the grafting efficiency.

References

1. T. L. Gresham, J. E. Jansen, and F. W. Shaver, *J. Am. Chem. Soc.*, **70**, 998, 999, 1001, 1003, 1004 (1948); *ibid.*, **72**, 72 (1950).

2. S. Okamura, T. Higashimura, and K. Tanaka, *Kogyo Kagaku Zasshi*, **65**, 707 (1962).

3. T. Kagiya, T. Sano, and K. Fukui, *Kogyo Kagaku Zasshi*, **67**, 951 (1964).

4. Y. Yamashita, Y. Ishikawa, and T. Tsuda, *Kogyo Kagaku Zasshi*, **66**, 104 (1963); *ibid.*, **66**, 110 (1963).

5. S. Inoue, T. Tomoi, T. Tsuruta, and J. Furukawa, *Makromol. Chem.*, **48**, 229 (1961).

6. G. C. Daul, R. M. Reinhardt, and J. D. Reid, *Textile Res. J.*, **24**, 738 (1954); *ibid.*, **25**, 330 (1955); *ibid.*, **26**, 1 (1956).

7. E. H. Nott and J. N. Grant, *Textile Res. J.*, **26**, 673 (1956).

8. N. Gokal and J. K. Skelly, *J. Soc. Dyers Colourists*, **75**, 486 (1959).

9. S. G. Cohen and H. C. Haas, *J. Am. Chem. Soc.*, **72**, 3954 (1950).

10. W. G. Rose and H. P. Lundgren, *Textile Res. J.*, **23**, 930 (1953).

11. C. Fearnley and J. B. Speakman, *J. Soc. Dyers Colourists*, **68**, 88 (1952).

12. T. Shiota, Y. Hiraki, Y. Goto, K. Hayashi, and S. Okamura, *Kobunshi Kagaku*, **22**, 252 (1965).

13. T. Shiota, Y. Goto, T. Ichida, S. Tazuke, and K. Hayashi, paper presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, 1965; *Abstracts of Papers*, p. 21.

14. H. H. Barbe and I. M. Koltboff, *J. Am. Chem. Soc.*, **50**, 1625 (1928).

15. E. R. Caley and C. W. Foulk, *J. Am. Chem. Soc.*, **51**, 1664 (1929).

16. T. Shiota, Y. Goto, and K. Hayashi, *J. Appl. Polymer Sci.*, **5**, 753 (1967).

17. S. Okamura, T. Higashimura, A. Tanaka, R. Kato, and Y. Kikuchi, *Makromol. Chem.*, **54**, 226 (1962).

18. T. Kagiya, T. Sano, and K. Fukui, *Kogyo Kagaku Zasshi*, **68**, 1141, 1144 (1965).

19. Y. Etienne and R. Soulas, in *Macromolecular Chemistry (J. Polymer Sci. C, 4)*, M. Magat, Ed., Interscience, New York, 1963, p. 1061.

Résumé

Le copolymère greffé de polyacrylonitrile–β-propiolactone (βPL) a été synthétisé au moyen de la polymérisation ionique dans laquelle la polymérisation de βPL était initée par du polyacrylonitrile contenant de faibles quantitiés de groupes réactionnels tels que COOK, COONa, COOLi, et COOH. L'electronégativité plus élevée cu cation de signe contraire favorise un degré de conversion final plus élevé et un pourcentage de greffage plus élevé également. Le pourcentage de greffage croit avec le temps de réaction et la concentration en groupes réactifs de polymères toncs, mais l'efficacité de greffage variait peu dans ces conditions. Dans la polymérisation en bloc à 60°C, l'efficacité de greffage est d'environ 60%, mais en solution au cours de polymérisation en solution dans le toluène ou le dioxane l'efficacité de greffage était plus élevée que dans la polymérisation en bloc ou dans le nitrobenzène.

Zusammenfassung

Ein Pfropfcopolymeres von β-Propiolacton (βPL) auf Polyacrylnitril wurde in einer durch Polyacrylnitril mit einer geringen Menge einer reaktiven Gruppe wie —COOK, —COONa, —COOLi oder —COOH angeregten ionischen Polymerisation synthetisiert. Eine höhere Elektronegativität des Gegenkations begüngstigte einen höheren Gesamtumsatz und eine höhere prozentuelle Pfropfung. Die prozentuelle Pfropfung nahm mit Reaktionsdauer und Konzentration an reaktiven Gruppen im Stammpolymeren zu, die Pfropfungsausbeute dagegen änderte sich unter idesen Bedingungen kaum. Bei der Polymerisation in Substanz bei 60°C betrug die Pfropfungsausbeute etwa 60%, sie war aber bei der Polymerisation in Toluol oder Dioxanlösung höher als in Substanz oder in Nitrobenzol.