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Ionic Graft Copolymerization. VII. Ionic Graft Copolymerization of β-Propiolactone onto the Trunk Polymers Containing Pyridine, Amide, Sulfonyl Chloride, and Carboxylic Acid Anhydride Groups

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Synopsis

The graft copolymerization of β-propiolactone (βPL) onto the various trunk polymers containing polar substituents such as pyridine, amide, sulfonyl chloride, and carboxylic acid anhydride groups was carried out. In the grafting onto the basic trunk polymer containing 4-vinylpyridine units, two kinds of grafting mechanism are supposed. In the case of rigorously dried trunk polymer, the polymerization is initiated by betaine and proceeds with higher grafting efficiency. Another is initiated by pyridinium hydroxide and proceeds with lower grafting efficiency in the presence of some amount of water. With acidic trunk polymer containing sulfonyl chloride groups, no graft copolymer was produced. The grafting efficiency of βPL onto the amphoteric trunk polymer containing acrylamide units was found to be between those of basic and acidic trunk polymer. In addition, the grafting by means of ionic copolymerization of βPL with maleic anhydride units contained in trunk polymer proceeded with very high grafting efficiency.

INTRODUCTION

Ionic graft copolymerization of β-propiolactone (βPL) has been investigated in detail as reported in the previous papers[1,2] of this series. In this paper, the graft copolymerizations of βPL onto the various trunk polymer containing 4-vinylpyridine (4VP), acrylamide (AAm), sulfonyl chloride, and maleic anhydride (MAH) units were examined.

The trunk polymer containing 4VP (4VP-trunk polymer) is considered as an anionic catalyst of the polymerization of βPL. The trunk polymer containing AAm (AAm-trunk polymer) has a tautomeric structure and so this is used as an amphoteric catalyst. The trunk polymer containing sulfonyl chloride groups (sulfonyl chloride-trunk polymer) is a cationic polymer catalyst. βPL was graft-copolymerized by these polymer catalysts. The trunk polymer containing MAH units (MAH-trunk polymer) is also reac-

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tive, which is copolymerized with βPL by anionic or cationic catalysts and results in a graft copolymer.

EXPERIMENTAL

Reagents

βPL and γ-butyrolactone were purified by the same way as shown in the previous paper.[1] 3,3-Bis(chloromethyl)oxetane (BCMO) was dried with CaH_2 followed by distillation under reduced pressure. Nitrobenzene and methylene chloride were purified by the usual procedures.

Preparation of Trunk Polymers

4VP-Trunk Polymer. 9 cc of 4VP was copolymerized with 1 cc of divinylbenzene (DVB) by 0.1 g of α,α′-azo-bis(isobutyronitrile) (AIBN) in 10 cc of benzene in vacuo at 60°C for 20 hr. Conversion was 88.0%, and 4VP content in the trunk polymer was calculated to be 8.9×10^{-3} mole/g from the elementary analysis.

AAm-Trunk Polymer. 3.26 g of AAm was copolymerized with 8 cc of styrene (St) and 2 cc of DVB by 0.130 g of benzoyl peroxide (BPO) in 26 cc of methanol in vacuo at 60°C for 16 hr. Conversion was 22.4%, and AAm content in this trunk polymer was calculated to be 1.09×10^{-3} mole/g trunk polymer from elementary analysis.

Sulfonyl Chloride-Trunk Polymer. 3 g of St–DVB copolymer was swollen with chloroform, reacted with 14 cc of chlorosulfonic acid at 0°C for 17 hr, washed with chloroform, and dried under reduced pressure.

MAH-Trunk Polymer. 10.4 g of St was copolymerized with 9.8 g of MAH by 0.1 g of BPO in 20 cc of benzene at 60°C for 24 hr in vacuo. Conversion was 98.0%, and MAH content in this trunk polymer was calculated to be 4.95×10^{-3} mole/g from elementary analysis.

Separation of Graft Copolymer

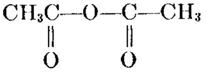
All trunk polymers used are insoluble in chloroform but homopolymer (poly-β-propiolactone) by-produced is easily dissolved. Therefore the graft copolymers were separated by extraction with chloroform.

RESULTS AND DISCUSSION

Polymerization of βPL by Various Catalysts

The trunk polymers containing 4VP, AAm, carboxyl chloride, sulfonyl chloride, and MAH are prepared as described above. It has been reported that βPL is polymerized easily by pyridine.[3,4] Polymerizations of βPL by the other catalysts such as propionamide, benzoyl chloride, propionyl chloride, toluenesulfonyl chloride, thionyl chloride, and acetic anhydride were carried out (Table I). And it was found that βPL was hardly polymerized by carboxyl chloride and acid anhydride under these conditions.

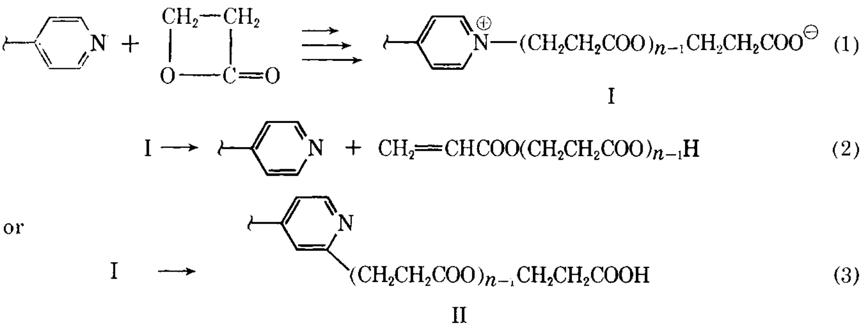
TABLE I
Polymerization of βPL by Various Catalysts[a]

Expt. no.	βPL, cc	Methylene chloride, cc	Catalyst, mg		Conversion, %
Y60-11	1	9	$C_2H_5CONH_2$	15	6.5
Y60-5	1	9	C_6H_5COCl	15	0
Y60-7	1	9	C_2H_5COCl	15	trace
Y60-3	1	9	$CH_3\phi SO_2Cl$	15	88.3
Y60-1	1	9	SO_2Cl_2	15	93.1
Y60-9	1	9	 $CH_3\underset{\underset{O}{\Vert}}{C}-O-\underset{\underset{O}{\Vert}}{C}-CH_3$	15	0

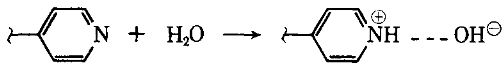
[a] Ten days, 30°C, in air.

Graft Copolymerization of βPL onto 4VP-Trunk Polymer

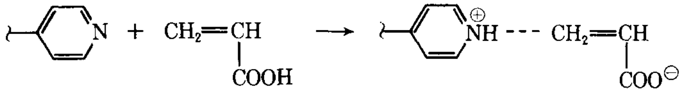
It is supposed that βPL is polymerized by pyridine in the following mechanisms[3,4]:



Compound I will be more unstable than compound II. But I is a homologue of pyridine betaine which was isolated as a relatively stable compound by Krüger et al.[5] So it is expected to graft copolymerize this monomer onto 4VP-trunk polymer by the mechanism shown by eq. (1) or (3). The trunk polymer was dried rigorously by heating at 98°C under reduced pressure, toluene solution of βPL was added in dry nitrogen stream, and then the reaction was carried out at 30°C (Fig. 1). This trunk polymer is classified as the same type of anionic catalyst as the trunk polymer containing sodium acrylate (ANa-trunk polymer) which was reported in the previous papers.[1,2] The grafting efficiency was estimated to be about 15 ~ 20%, and this is lower than that of ANa-trunk polymer (about 65%).[1] In the case of ANa-trunk polymer, the grafting efficiency decreases by the chain transfer to monomer or impurity in the system; but in the case of 4VP-trunk polymer, besides chain transfer, the grafting efficiency decreases by the termination reaction as shown in eq. (2) and the initiation reaction indicated by eqs. (4) and (5):



(4)



(5)

4VP-trunk polymer is hydroscopic. When 4VP-trunk polymer was not dried before using, βPL was polymerized quickly but hardly graft copolymerized, because the polymerization is initiated by OH^- as shown in eq. (4) and Figure 2.

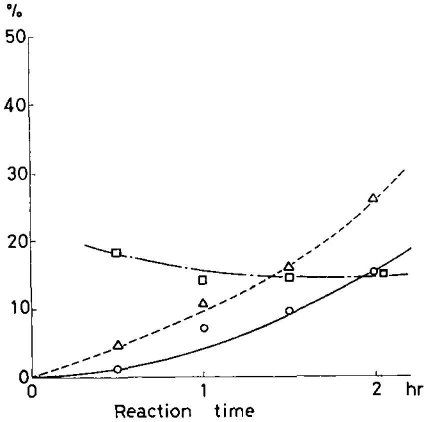


Fig. 1. Graft copolymerization of βPL onto 4VP-trunk polymer. Trunk polymer was dried rigorously at 98°C under high vacuum and then reacted in nitrogen. Trunk polymer, 0.1 g; 4VP content, 8.9×10^{-3} mole/g trunk polymer; βPL, 1 cc; toluene, 4 cc; temperature, 30°C; in air: (—○—) total conversion; (—·□·—) grafting efficiency; (— —△— —) % grafting.

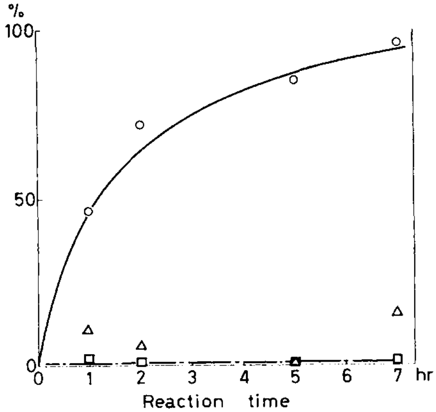


Fig. 2. Graft copolymerization of βPL onto 4VP-trunk polymer. Trunk polymer was used without drying. Trunk polymer, 0.1 g; 4VP content, 8.9×10^{-3} mole/g trunk polymer; βPL, 1 cc; toluene, 4 cc; temperature, 30°C; in air: (——○——) total conversion; (—·□·—) grating efficiency; (——△——) % grafting.

Graft Copolymerization of βPL onto AAm-Trunk Polymer

Similar graft copolymerization, that is, ethylene oxide onto polyamide, has been reported by Haas et al.,[6] Miller et al.,[7] and Rafikov et al.[8] In this paper, βPL was graft copolymerized onto AAm-trunk polymer (Fig. 3). The total conversion and the per cent grafting increase with reaction time, but the grafting efficiency decreases to ~30–40%. In a previous paper[2] it was demonstrated that the grafting efficiency increases with the extent of basicity of the trunk polymer; the grafting efficiency of βPL onto the anionic active trunk polymer (ANa-trunk polymer) was 65%, but that onto the cationic active trunk polymer was estimated to be only a few per cent.

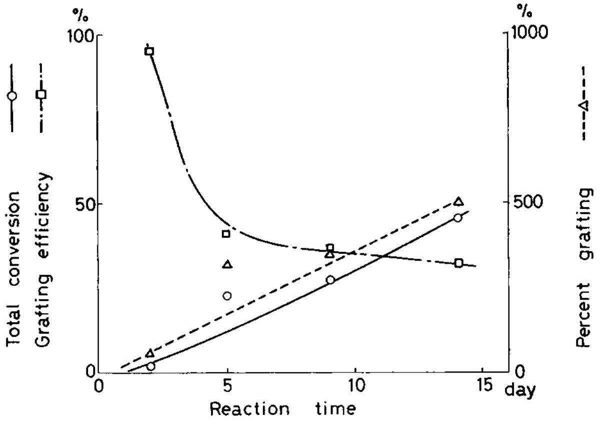


Fig. 3. Graft copolymerization of βPL onto AAm-trunk polymer. Trunk polymer, 0.1 g; AAm content, 1.09×10^{-3} mole/g trunk polymer; βPL, 3 cc; temperature, 60°C; in air.

TABLE II

Effect of Reaction Temperature on the Graft Copolymerization of βPL onto AAm-Trunk Polymer[a]

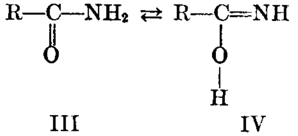
Exp. no.	Reaction temp., °C	Reaction time, hr	Total conv., %	Per cent grafting, %	Grafting efficiency, %
I 8-5	60	48	1.7	55.1	94.8
I 9-6	60	120	22.2	317.0	41.4
I 8-7	60	216	27.1	346.1	36.8
I 8-8	60	336	45.1	496.8	31.7
I 8-1	80	3	0.4	9.3	83.0
I 8-10	90	3	0.9	29.0	96.7
I 8-2	100	3	3.1	103.2	94.8
I 8-3	120	3	21.0	304.5	41.8
I 8-4	140	3	55.6	398.0	20.6

[a] Trunk polymer, 0.1 g; AAm content, 1.09×10^{-3} mole/g trunk polymer; βPL, 3 cc; in vacuo.

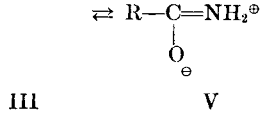
The grafting efficiency onto AAm-trunk polymer has a medium value between anionic and cationic active trunk polymer. In this system, the lower reaction temperature favors the higher grafting efficiency (Table II). In the infrared spectrum of graft copolymer, the absorption bands corresponding to both trunk polymer (NH, 3400 cm^{-1}, 3500 cm^{-1}; primary amide C=O, 1685 cm^{-1}; phenyl, 3010 cm^{-1}, 1600 cm^{-1}) and branched polymer (ester C=O, 1740 cm^{-1}; ether, 1170 cm^{-1}) were observed.

Polymerization of βPL by Various Amide Derivatives

The amide is a tautomer[9] and has a resonance structure[10] as shown in eq. (6):

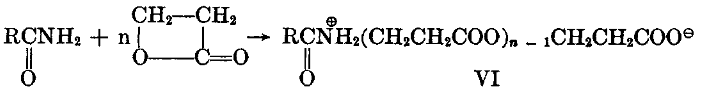


$$\underset{\text{III}}{R-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2} \rightleftarrows \underset{\text{IV}}{R-C(-O-H)=NH} \qquad (6)$$

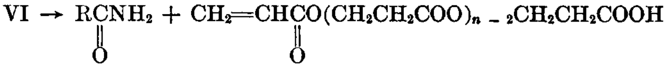


$$\underset{\text{III}}{} \rightleftarrows \underset{\text{V}}{R-C(-O^{\ominus})=NH_2^{\oplus}} \qquad (7)$$

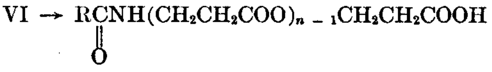
Two kinds of polymerization mechanisms are as follows: polymerizations of βPL by basic nitrogen of keto form (III) (mechanisms A), and acidic hydroxy group of imidohydrin form (IV) or a resonance structure (V) (mechanisms B). The latter seems to be improbable because of the very weak acidity of amide.



$$RC(=O)NH_2 + n\,\begin{array}{c}CH_2-CH_2\\ |\qquad\ \ |\\ O-C=O\end{array} \rightarrow \underset{\text{VI}}{RC(=O)\overset{\oplus}{N}H_2(CH_2CH_2COO)_{n-1}CH_2CH_2COO^{\ominus}} \qquad (8)$$



$$\text{VI} \rightarrow RC(=O)NH_2 + CH_2{=}CHC(=O)O(CH_2CH_2COO)_{n-2}CH_2CH_2COOH \qquad (9)$$



$$\text{VI} \rightarrow RC(=O)NH(CH_2CH_2COO)_{n-1}CH_2CH_2COOH \qquad (10)$$

It is supposed that the active species (VI) has a cyclic structure by the formation of an intramolecular ion pair. Homopolymer might be obtained by reaction (9) or chain transfer reaction to monomer and graft copolymer by reaction (8) or (10). The polymerizations of βPL by various amide derivatives were carried out for the purpose of the investigation of polymerization mechanisms. The polymerizations of βPL by N-substituted amides of various carboxylic acids are shown in Figure 4a and Figure 4b, respectively. It was found that the rate of polymerization increases in the following order: $CH_3CONEt_2 > CH_3CONHEt > CH_3CONH_2 > CH_2{=}CHCONH_2 \approx (CH_3)_2CHCONH_2 > C_6H_6CONH_2 \approx CH_3CONH(C_6H_4)OCH_3 > CH_3CONH(C_6H_5)$.

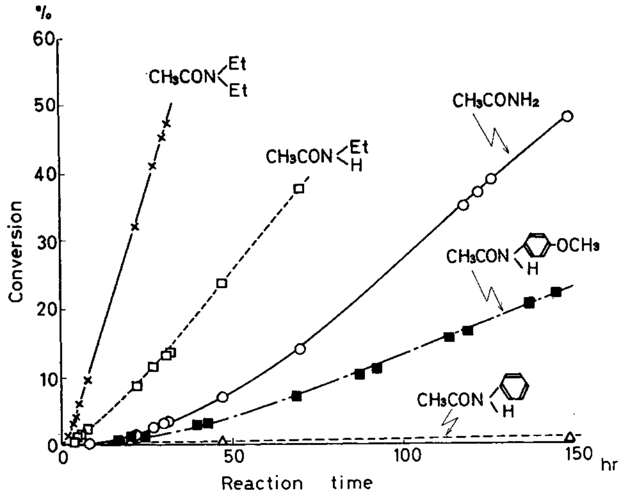


Fig. 4a. Polymerization of βPL by various N-substituted acetamides by dilatometry. βPL, 3 cc; catalyst, 3.7 × 10^{-2} mole/l.; temperature, 60°C; in air.

On the other hand, the electronegativity of substituted groups increases in the following order[11]: C_6H_5— > CH_2=CH— > H— > CH_3— > C_2H_5—. Considering the role of the substituents connected with the nitrogen atom in catalytic action, it is concluded that the higher electronegative groups are substituted (that is, the lower is the basicity of nitrogen atom), the lower the polymerization activity becomes. That is, this activity is observed as CH_3CONEt_2 > $CH_3CONHEt$ > CH_3CONH_2 > $CH_3CONHC_6H_5$ (Fig. 4a).

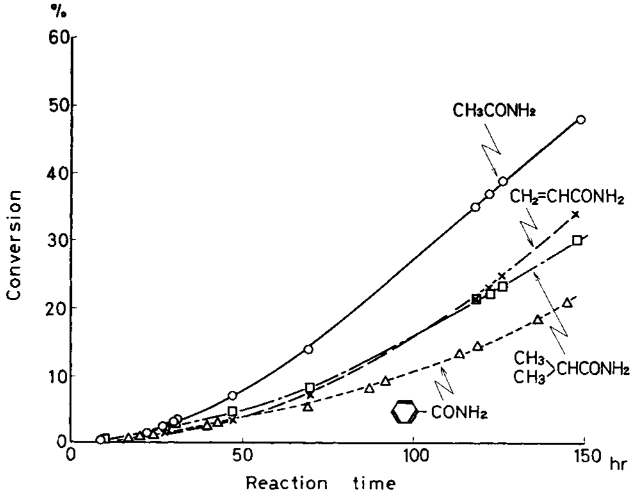


Fig. 4b. Polymerization of βPL by various acid amides by dilatometry. βPL, 3 cc; catalyst, 3.7 × 10^{-2} mole/l.; temperature, 60°C; in air.

Because βPL is polymerized even by N-diethylacetamide which has no active hydrogen atom, the polymerization mechanism by active hydrogen on the nitrogen atom should be rejected. The low catalytic activity of acetanilide is due to the steric hindrance by the phenyl group connected with the nitrogen atom and the resonance stability[12] of form IV or V. The unexpectedly low catalytic activity of *p*-methoxybenzanilide in spite of the high electron-donating nature of the methoxy group is also caused by steric hindrance of the phenyl group and resonance stability of form IV or V.

About the effect of the acyl group in the amide compound on catalytic action, it was found that the higher electronegativity of the acyl group and the larger the resonance structure of IV or V, the lower the polymerization activity. It is estimated in the following order: $CH_3CONH_2 > CH_2{=}CHCONH_2 \approx (CH_3)_2CHCONH_2 > C_6H_5CONH_2$. The catalytic activity of isobutylamide for the polymerization of βPL could not be well explained by electronegativity, and this may be caused by a steric effect.

Summarizing the experimental results, the following supports the polymerization mechanisms by the basic nitrogen atom of amide group, eqs, (8), (9), and (10): (1) the larger the electron-donating nature of the substituent on the nitrogen atom of amide, the larger the catalytic activity in the polymerization of βPL. (2) Even the amide without active hydrogen atom on the nitrogen atom has a catalytic activity for the polymerization of βPL. (3) If the polymerization of βPL proceeds according to mechanism B, the larger the contribution of the resonance structure of substituent on the nitrogen atom in the amide, the higher the catalytic activity. However, the experimental results indicate that mechanism A is preferable. The grafting efficiency depends upon the behavior of the hydrogen atom abstructed in the termination reaction. It seems that in form VI the hydrogen atom on the $-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\oplus}{\mathrm{N}}\mathrm{H}_2-$ group will be removed as a proton more easily than that on $-\mathrm{CH}_2-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-$ because of the excess positive charge on the $-\overset{\oplus}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}}-\mathrm{NH}_2-$ group. That is, reaction (10) should be predominant. However, the grafting efficiency as shown in Figure 3 is limited to 30% and this indicates that a chain transfer reaction to monomer coexists besides eq. (10).

Graft Copolymerization of βPL onto Sulfonyl Chloride-Trunk Polymer

Graft copolymerization of βPL, N-vinylcarbazole (NVCZ); and α-methylstyrene (α-MeSt) onto sulfonyl chloride-trunk polymer is shown in Table III. In these runs, the graft copolymers were not obtained.

TABLE III

Graft Copolymerization of βPL onto the Trunk Polymer Containing —SO_2Cl[a]

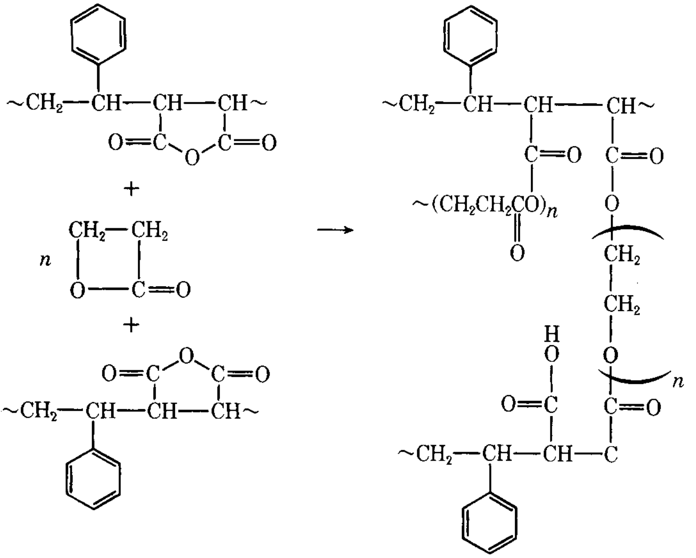
Exp. no.	Monomer, g		Toluene, cc	Temp., °C	Time, min	Total conv., %	Polymer,[b] g
I 153-1	βPL	1.16	4.0	60	60	76.6	0.0993
I 153-5	NVCZ	0.50	4.0	30	5	80.5	0.0845
I 153-6	αMeSt	1.00	4.0	60	60	1.8	0.0907

[a] Chlorosulfonated St–DVB copolymer, 0.1 g; —SO_2Cl content, 7.3 × 10^{-3} mole/g trunk polymer; in air.

[b] Polymer after extraction of homopolymer.

Graft Copolymerization of βPL onto MAH-Trunk Polymer

A crosslinked graft copolymer was synthesized by means of ionic copolymerization in which βPL was copolymerized with cyclic carboxylic acid anhydride contained in the MAH-trunk polymer as shown in eq. (11):



(11)

The various graftings with and without ionic catalyst are shown in Figures 5 and 6 and Table IV, respectively. In Figure 6, the grafting behavior is investigated by dilatometry and viscometry. In this reaction system, gel formation took place rapidly within 15 min. In the case of MAH-trunk polymer this gel formation was made in the solution of βPL but not in γ-butyrolactone (Table V). This demonstrates that crosslinking reaction does not take place by the mutual reaction between the trunk polymers as shown in eq. (12). The grafting efficiency in the presence of βPL was very high in the case of grafting without catalyst in bulk, as shown in Figure 5.

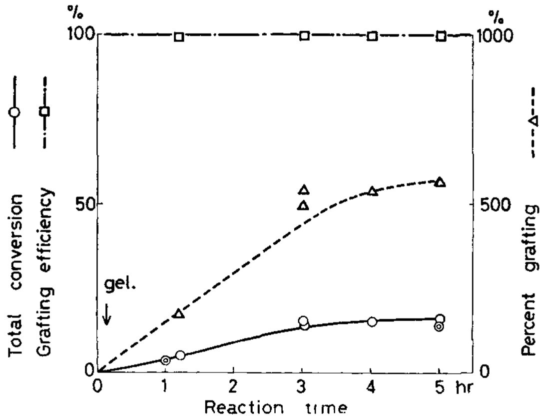


Fig. 5. Graft copolymerization of βPL onto MAH-trunk polymer in bulk. Trunk polymer, 0.1 g; MAH content, 4.95 × 10^{-3} mole/g trunk polymer; βPL, 3 cc; temperature, 120°C: (○) conversion of succinic anhydride-catalyzed polymerization.

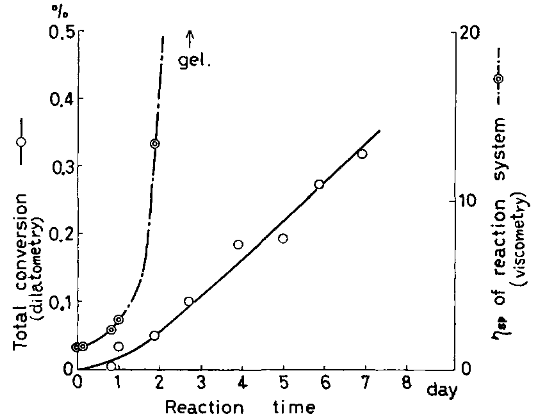


Fig. 6. Graft copolymerization of βPL onto MAH-trunk polymer. Trunk polymer, 0.1 g; MAH content, 4.95 × 10^{-3} mole/g trunk polymer; βPL, 10 cc; temperature 60°C; in air.

The possibility of grafting by the reaction of MAH-trunk polymer with βPL homopolymer was investigated in comparison with that of βPL onto MAH-trunk polymer (Table VI). The grafting efficiency in this reaction

TABLE IV

Graft Copolymerization of βPL onto MAH-Trunk Polymer by CH_3COONa or $CH_3(C_6H_5)SO_3H$[a]

Exp. no.	Catalyst, mole		Reaction time	Total conversion, %	Per cent grafting, %	Grafting efficiency, %
G130-1	CH_3COONa	4.4 × 10^{-4}	20 hr	32.0	338.0	91.2
G129-1	$CH_3\phi SO_3H$	4.4 × 10^{-4}	10 min	27.7	231.0	72.2
G129-2	$CH_3\phi SO_3H$	4.4 × 10^{-4}	3 hr	33.5	293.5	75.8

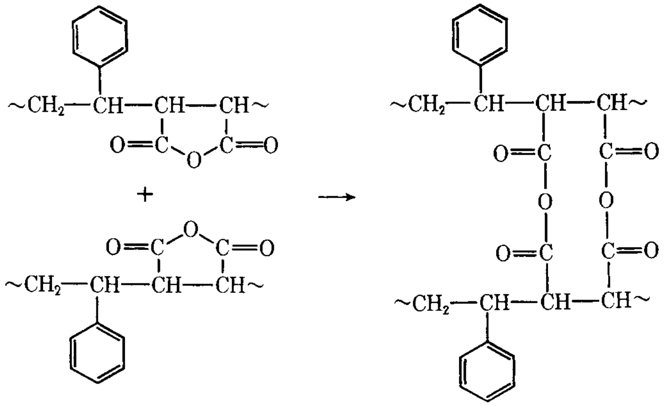
[a] St–MAH copolymer, 0.1 g; MAH content, 4.95 × 10^{-3} mole/g trunk polymer (50 mole-%); βPL, 1 cc; nitrobenzene, 4 cc; 60°C; in air.

TABLE V

Viscosity Change of St–MAH Copolymer Solution by Heating in βPL or γ-Butyrolactone

Exp. no.	St–MAH copolymer, g	βPL, cc	γ-Butyrolactone, cc	Temp., °C	Viscosity[a] at indicated reaction times: 0	15 min	45 min	4 hr
I 50-1	0.1	3	0	120	7.9 sec	∞	∞	∞
I 50-2	0.1	0	3	120	21.7 sec	19.1 sec	23.0 sec	21.5 sec

[a] Viscosity is shown as the falling time of a small ball (0.27 g, 0.4 cm diameter) through a distance of 5 cm.


(12)

between those polymers was as low as ~2–3%. This result suggests that the grafting reaction is initiated by the anhydride group of the trunk polymer.

Solubility of the trunk polymer, PβPL, and the graft copolymer (per cent grafting, 500%) is exhibited in Table VII. The graft copolymer was not completely dissolved in acetone in which both trunk polymer and PβPL homopolymer are soluble. But this graft copolymer dissolved in acetone containing 1% H_2O, and this H_2O amount corresponds to more than 100 times the MAH units in the trunk polymer. These facts demonstrate the existence of the polymer crosslinked by carboxylic acid anhydride bonds (eq. (11)). In the infrared spectrum of the graft copolymer of βPL onto the MAH-trunk polymer, the absorptions of MAH units (1780 and 1860 cm^{-1}), styrene units (1500, 1600, and 3010 cm^{-1}) and βPL units (1740 cm^{-1}) were observed.

TABLE VI

Graft Copolymerization by Reaction of MAH-Trunk Polymer with PβPL[a]

Exp. no.	Temp., °C	Time, hr	Per cent grafting, %	Grafting efficiency, %
I 12-1	120	1	7.0	2.3
I 12-2	120	3	7.3	2.4

[a] Trunk polymer, 0.1 g; PβPL, 0.3 g; γ-butyrolactone, 2.7 cc as a solvent.

TABLE VII
Solubility of Trunk Polymer, PβPL, and Graft Copolymer[a]

	St–MAH copolymer	PβPL	Graft copolymer
Water	X	X	X
Methanol	X	X	X
Toluene	X	X	X
Chloroform	X	●	X
Dioxane	Δ	●	Δ
Nitrobenzene	Δ	●	Δ
Dry acetone	●	●	Δ
Acetone 10 cc + water 0.1 cc	●	●	○

[a] (●) very soluble; (○) soluble; (Δ) partly soluble; (X) insoluble; at 60°C.

CONCLUSION

Ionic graft copolymerizations of βPL onto the various trunk polymers containing polar substituents were carried out. When the 4VP-trunk polymer used was completely dried, the grafting proceeded with high grafting efficiency. But when the trunk polymer was insufficiently dried, the grafting efficiency was very low. These results were interpreted by two polymerization mechanisms initiated by betaine and by pyridinium hydroxide, respectively. In the grafting onto AAm-trunk polymer, the grafting efficiency decreased to about 30–40% with increased reaction time. Catalytic activities of the various amide derivatives in the polymerization of βPL were compared with one another. High electron-donating groups on the nitrogen atom and low resonance stability in amide resonance favor higher catalytic activity in the polymerization of βPL.

The graft copolymerization of βPL onto MAH-trunk polymer proceeded with very high grafting efficiency and the crosslinked graft copolymer was produced.

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