

Ionic Graft Copolymerization. VIII. Homopolymerization of β -Propiolactone by Radical Catalysts in the Presence of Electron Acceptors and Application to Graft Copolymerization

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Synopsis

The polymerization of β -propiolactone (β PL) induced by radiation and by radical catalysts, the influences of radical inhibitors and electron acceptors on this polymerization, and graft copolymerization were studied. It was found that β PL was polymerized by benzoyl peroxide in the presence of electron acceptors such as maleic anhydride and acrylonitrile. This polymerization method was applied to graft copolymerization. The electron donative trunk polymer containing ether groups was heated with benzoyl peroxide or was irradiated by γ -rays from Co^{60} in the presence of maleic anhydride as the electron acceptor. β PL was added subsequently to form the graft copolymer.

INTRODUCTION

It has been reported by Ohse et al.¹ that β -propiolactone (β PL), purified under severe conditions by using toluene diisocyanate as the dehydrating agent, is polymerized by radical catalysts such as benzoyl peroxide (BPO) or α, α' azo-bis-isobutyro-nitrile (AIBN). In previous works,²⁻⁴ the ionic graft copolymerization of β PL has been investigated. In this paper the following subjects were investigated for the purpose of understanding the graft copolymerization of β PL by radical catalysts.

1. Homopolymerization of β PL by radical catalysts.
2. Radiation induced homopolymerization of β PL in liquid state.
3. Homopolymerization of β PL by radical inhibitors.
4. Homopolymerization of β PL by radical catalysts in the presence of radical inhibitors.
5. Homopolymerization of β PL by radical catalysts in the presence of electron acceptors.
6. Graft copolymerization of β PL onto an electron donative trunk polymer.

Different polymerization behaviors were observed for β PL purified by various methods. β PL purified by calcium chloride was not polymerized

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by radical catalysts. On the other hand that purified by toluene diisocyanate was polymerized and the reaction mixture developed a deep orange colour. By adding a small amount of toluene diisocyanate the former β PI, was polymerized by BPO with the same colour as the latter case. The former β PL was polymerized by AIBN and this polymerization was not inhibited by oxygen or radical inhibitors as observed in usual radical polymerization but rather was accelerated. These results are similar to the polymerization of cyclic ethers by radical catalysts in the presence of electron acceptors such as maleic anhydride (MAH), which is reported by Takakura et al.⁵ In this case, toluene diisocyanate and radical inhibitors may act as an electron acceptor. Therefore, the former β PL was polymerized by radical catalysts in the presence of various electron acceptors and this polymerization method was applied to graft copolymerization.

EXPERIMENTAL

Reagents

The purity of β PL dried by calcium hydride, calcium chloride and toluene diisocyanate is compared in Table I. β PL purified by calcium chloride

TABLE I
Purity of β PL Purified by Various Methods

	Crude β PL	β PL purified by CaH ₂	β PL purified by CaCl ₂	β PL purified by toluene diisocyanate
β PL content (%)	96.6	99.84 \pm 0.05	99.95 \pm 0.05	99.84 \pm 0.05
acrylic acid content (%)	0.90	0.098 \pm 0.0005	0.062 \pm 0.0005	0.43 \pm 0.005
Water content (ppm)	4150	300 ~ 600	<10	<10

was the most pure one in this series. Therefore, β PL purified by calcium chloride was mainly used here and only in part of the experiments was the monomer purified by toluene diisocyanate employed. *N*-vinyl carbazole (NVCZ) was recrystallized three times from *n*-hexane solution. Acrylonitrile (AN) was passed through a silica-gel tube in a nitrogen stream and then distilled under reduced pressure. BPO was reprecipitated three times from its chloroform solution by the addition of methanol as precipitant. AIBN was recrystallized three times from methanol solution. Benzoquinone (BQ), 1,1-diphenyl-2-picryl-hydrazyl (DPPH), *m*-dinitrobenzene, chloranil and MAH were recrystallized three times from petroleum ether, ethyl ether, ethanol, benzene and chloroform solution, respectively.

Purification of β PL and Determination of Purity

Purification by Calcium Hydride.⁶ Crude β PL was dried by calcium hydride for 3 days followed by distillation under reduced pressure.

Purification by Calcium Chloride.⁶ Crude β PL was passed quickly through calcium chloride twice, followed by distillation under reduced pressure.

Purification by Toluene Diisocyanate.¹ Crude β PL containing 1% of toluene diisocyanate was distilled carefully under reduced pressure.

Determination of Water Content. The water content was determined by the Karl Fischer method.

Determination of β PL Content.⁷ β PL was allowed to react with excess thiosulfate solution and unchanged thiosulfate was titrated by standard iodine solution.

Determination of Acrylic Acid in β PL.⁷ Acrylic acid in β PL was brominated with potassium bromate-potassium bromide mixture in aqueous solution and unchanged bromine was titrated by standard thiosulfate solution.

Preparation of Trunk Polymers

Polyethylene Glycol (PEG). Commercial PEG was reprecipitated from acetone solution three times by addition of *n*-hexane.

Polyoxymethylene (POM). 2 g of trioxane (TOX) was polymerized by 2×10^{-4} mole of BF_3OEt_2 in 8 cc of dichlorethane in a nitrogen stream at 60°C for 48 hr. The polymer obtained was washed with methanol.

Poly-3,3-bis(chloromethyl)cyclooxabutane (PBCMO). 5 cc of 3,3-bis(chloromethyl)cyclooxabutane (BCMO) was polymerized at 30°C for 5 min by adding 0.5 cc of BF_3OEt_2 -toluene solution (0.66 mole/l) to the monomer. The polymer obtained was dissolved in cyclohexanone and reprecipitated by methanol as precipitant.

Isobutyl vinyl ether (IBVE)-Divinyl benzene (DVB) copolymer. 7 cc of IBVE was copolymerized with 0.78 cc of DVB by 100 mg of BPO dissolved in 8 cc of benzene at 60°C for 3 days in vacuo.

IBVE-Styrene (St) Copolymer. 3 cc of IBVE was copolymerized with 7 cc of St by 100 mg of BPO in 8 cc of benzene.

Poly-N-Vinyl Carbazole (PNVCZ). 5 g of NVCZ was polymerized by 50 mg of BPO in 5 cc of benzene at 60°C for 116 hr in vacuo.

St-MAH copolymer. 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.

Polymerization Procedure

Radiation Induced Polymerization in the Liquid State. 1 cc of β PL was degassed by using a high vacuum technique and then irradiated by γ -rays from a Co^{60} source.

Radiation Induced Graft Copolymerization. Polypropylene was irradiated by γ -rays in air to produce the polymer peroxide. 0.1 g of pre-irradiated polypropylene was heated subsequently in the presence of 1 cc of β PL in vacuo.

Polymerization by Radical Catalysts or Compounds Classified as Radical Inhibitor. It is well known⁸ that β PL is polymerized easily even by very

TABLE II
Radiation Induced Polymerization of β PL in Liquid State^a

Experiment no.	Temp., °C	Time, hr	Dose rate, r/hr	Total dose, r	Conversion, %			
					Irradiation		Thermal polymerization	
					Insoluble polymer in CH ₃ OH	Residual polymer after evaporation	Insoluble polymer in CH ₃ OH	Residual polymer after evaporation
G 13-1	60	26.1	9×10^3	2.3×10^5	0	1.5	0	1.7
G 13-2	80	7.0	9×10^3	0.63×10^5	0	2.5	0	2.1
G 13-3	80	24.0	9×10^3	2.2×10^5	0.8	7.3	3.9	8.5
G 13-4	80	47.7	9×10^3	4.3×10^5	2.5	10.2	12.2	22.0
G 13-5	100	24.0	9×10^3	2.2×10^5	20.7	44.7	19.5	26.6

^a β PL, 1 cc; in vacuo. β PL was purified with CaCl₂.

weak ionic catalysts such as sodium chloride and sodium bromide. Therefore some radical inhibitors act as a weak ionic catalyst and β PL might be polymerized by an ionic mechanism. 1 cc of β PL was polymerized in vacuo by 5×10^{-5} mole of radical catalysts or radical inhibitors.

Polymerization by Radical Catalysts in the Presence of Electron Acceptors. 1 cc of β PL was polymerized by 5×10^{-5} mole of BPO in the presence of 1.61×10^{-4} mole of electron acceptors such as AN, MAH, chloranile and *m*-dinitrobenzene in air.

Graft Copolymerization by Donor-Acceptor Complex. Graft copolymerization of β PL onto electron donative trunk polymers in the presence of the electron acceptor (MAH) was carried out by initiation with either BPO or irradiation with γ -rays. The details of reaction conditions are shown in Tables XI and XII.

RESULTS AND DISCUSSION

Radiation Induced Polymerization of β PL in the Liquid State If β PL polymerizes by a radical mechanism, then radiation induced polymerization should proceed in the liquid state. Then liquid β PL was irradiated and this was compared with thermal polymerization (Table II). The conversion in radiation induced polymerization of β PL at high temperature consists of two parts of thermal and radiation induced polymerization. But this result unexpectedly was comparable with or rather lower than that in thermal polymerization. In consideration of this result, the evidence of radiation induced radical polymerization was not obtained.

Radiation Induced Graft Copolymerization of β PL onto Preirradiated Polypropylene

It is well known that graft copolymerization is performed by the so called preirradiation method. That is, the polymer is irradiated in air to form polymer peroxide. Then this is heated subsequently in the presence of monomer which is polymerizable by a radical mechanism. If β PL could be polymerized by a radical mechanism, then a graft copolymer should be obtainable by thermal decomposition of polypropylene peroxide (formed by preirradiation) in the presence of β PL. Therefore, the possibility of radiation induced grafting was investigated (Table III), but not graft copolymer was observed.

Polymerization of β PL by some Radical Catalysts

β PL was polymerized in bulk by radical catalysts such as BPO, AIBN and cummene hydroperoxide (CHP) (Table IV, Fig. 1). The rate of polymerization by AIBN is higher than that of thermal polymerization, but in the case of CHP or BPO there are no clear differences from thermal polymerization. Ohse et al. reported¹ that β PL purified by toluene diisocyanate was polymerized by either BPO or AIBN. The contradiction between these results is due to the difference of purification method. Polymeriza-

TABLE III
Graft Copolymerization of β PL onto Preirradiated Polypropylene

Experiment no.	Preirradiation			Grafting			Total ^a conv., %	Percent grafting, %	
	Atmo- sphere	Temp., °C	Dose rate, r/hr	Total dose, r	Atmo- sphere	Temp., °C			Time, day
I-3001	in air	30	2.3×10^4	2.3×10^6	in vacuo	80	1	11.3	0
I-3002	in air	30	2.3×10^4	2.3×10^6	in vacuo	100	1	10.7	0

Trunk polymer (polypropylene fiber), 0.1 gr; β PL (purified by CaCl_2), 1 cc.

^a Total conversion was determined by weighing residual polymer after evaporation.

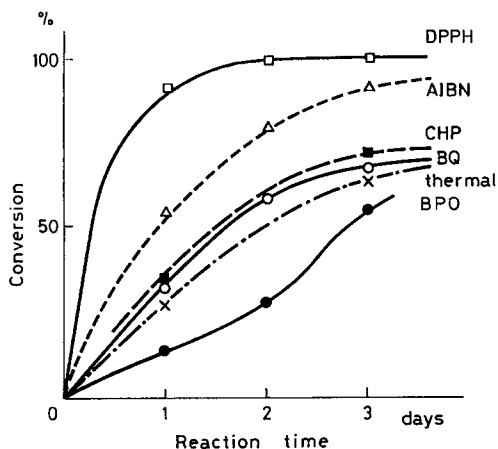


Fig. 1. Polymerization of β PL by radical catalysts or radical inhibitors. β PL, 1 cc; catalyst, 5×10^{-5} mole; in vacuo, at 100°C .

tion (initiated by BPO) of β PL purified by various methods are compared in Table V. Only β PL purified by toluene diisocyanate was polymerized with a color of deep orange, but β PL purified by calcium chloride was also

TABLE IV
Polymerization of β PL by Radical Catalysts^a

Catalyst, mg	Temp., $^\circ\text{C}$	Time	Conversion (%)	
			Insoluble polymer in CH_3OH	Residual polymer after evaporation
BPO 12.1	80	1 day	1	9
BPO 12.1	100	1 day	11	13
BPO 12.1	100	2 day	16	28
BPO 12.1	100	3 day	36	55
BPO 12.1	120	1 hr	0	5
BPO 12.1	120	2 hr	5	8
BPO 12.1	120	3 hr	10	16
AIBN 8.2	80	1 day	14	16
AIBN 8.2	100	1 day	46	54
AIBN 8.2	100	2 day	71	80
AIBN 8.2	100	3 day	83	92
CHP 7.6	100	1 day	31	34
CHP 7.6	100	3 day	65	72
Thermal	80	1 day	4	9
Thermal	100	1 day	20	27
Thermal	100	3 day	40	64
Thermal	120	1 hr	0	4
Thermal	120	2 hr	7	10
Thermal	120	3 hr	15	18

^a β PL, 1 cc; catalyst, 5×10^{-5} mole.

polymerized in the presence of a small amount of toluene diisocyanate with the same color (Table VI). These results are explained by a mechanism similar to the polymerization of cyclic ether by BPO in the presence of MAH.⁵ Toluene diisocyanate may act as an electron acceptor in this case.

TABLE V
Polymerization of β PL Purified by Various Methods^a

Catalyst	Temp., °C	Time, hr	Purification method of monomer	Con- version, %	Color
Thermal	80	24	CaCl ₂	4	Colorless
Thermal	80	24	CaH ₂	6	Colorless
Thermal	80	24	CH ₃ φ(NCO) ₂	6	Colorless
Thermal	80	24	CH ₃ φ(NCO) ₂ (Ohse's data)	4	—
BPO					
12.1 mg	80	24	CaCl ₂	1	Colorless
12.1 mg	80	24	CaH ₂	0	Colorless
12.1 mg	80	24	CH ₃ φ(NCO) ₂	37	Orange
12.1 mg	80	24	CH ₃ φ(NCO) ₂ (Ohse's data)	15	—

^a β PL, 1 cc; in vacuo.

TABLE VI
Polymerization of β PL by BPO in the Presence of Toluene Diisocyanate^a

Experiment No.	β PL, cc	Toluene diisocy- anate, mg	BPO, mg	Temp., °C	Time, hr	Con- version, %	Remark
I 200-1	3	0	0	83	27	0	Colorless
I 200-2	3	0	36	83	27	0	Colorless
I 200-3	3	15	0	83	27	trace	Slightly orange
I 200-4	3	15	36	83	27	41.4	Orange

^a In air, in dark.

Polymerization of β PL by Some Radical Inhibitors

β PL might be polymerized in the presence of radical inhibitors which act as electron acceptors. Therefore, such radical inhibitors as BQ, DPPH, picric acid, and *m*-dinitrobenzene were studied to see if they could initiate polymerization of β PL (Table VII, Fig. 1). DPPH and picric acid initiated the polymerization of β PL, but BQ and *m*-dinitrobenzene did not. In the consequence, BQ and *m*-dinitrobenzene could be used as radical inhibitors in the polymerization of β PL.

TABLE VII
 Polymerization of β PL by Radical Inhibitors*

Catalyst, mg	Atmosphere	Temp., °C	Time	Conversion, %		Color
				Insoluble polymer in CH ₃ OH	Residual polymer after evaporation	
BQ 5.4	vacuo	80	1 day	11	15	Light yellow
BQ 5.4	vacuo	100	1 day	27	32	Light yellow
BQ 5.4	vacuo	100	2 day	47	59	Light yellow
BQ 5.4	vacuo	100	3 day	41	67	Light yellow
DPPH 19.7	vacuo	100	3 hr	0	—	Dark purple
DPPH 19.7	vacuo	100	1 day	86	93	Dark purple
DPPH 19.7	vacuo	100	2 day	92	101	Dark purple
DPPH 19.7	vacuo	100	3 day	91	101	Dark purple
DPPH 19.7	vacuo	120	3 hr 15 min	82	—	Dark purple
DPPH 19.7	air	60	3 day	0	—	Dark purple
DPPH 19.7	air	100	3 hr	0	—	Dark purple
DPPH 19.7	air	120	3 hr	87	—	Dark purple
DPPH 19.7	air	120	3 hr 15 min	86	—	Dark purple
Picric acid 30	air	60	3 day	25	—	Yellow
Picric acid 30	air	120	3 hr	50	—	Purple → brown
Dinitrobenzene 30	air	60	3 day	0	—	Light yellow
Dinitrobenzene 30	air	120	3 hr	8	—	Light yellow

 * β PL purified by CaCl₂, 1 cc; catalyst, 5×10^{-5} mole.

**Polymerization of β PL by AIBN in the
Presence of Radical Inhibitors**

Effects of air or radical inhibitors on the polymerization of β PL by AIBN were investigated. As shown in Table VIII and IX, the polymer-

TABLE VIII
Effect of Air on the Polymerization of β PL Catalyzed by AIBN^a

Catalyst mg	Atmo- sphere	Time, day	Conversion, %	Color
AIBN 8.2	vacuo	1	43-46	Light yellow
AIBN 8.2	vacuo	3	83-85	Light yellow
AIBN 8.2	air	1	46	Light yellow
AIBN 8.2	air	3	87	Light yellow
Thermal	vacuo	1	20	Colorless
Thermal	vacuo	3	56	Colorless

^a β PL, 1 cc; at 100°C.

TABLE IX
Effect of the Presence of a Radical Inhibitor on the Polymerization by AIBN^a

Catalyst, mg	Radical inhibitor, mg	Time, day	Conversion, %	Color
AIBN 8.2	0	1	43-46	Light yellow
AIBN 8.2	0	3	83-85	Light yellow
AIBN 8.2	C ₆ H ₄ (NO ₂) ₂ 16.8	1	53	Light yellow
AIBN 8.2	16.8	3	84	Light yellow
AIBN 8.2	C ₆ H ₄ (NO ₂) ₂ 33.6	3	89	Light yellow
Thermal	0	1	20	Colorless
Thermal	0	3	56	Colorless

^a β PL, 1 cc; in vacuo; at 100°C.

ization was not inhibited by addition of air or *m*-dinitrobenzene but, on the contrary, was accelerated slightly. In the polymerization of β PL by radical catalysts, toluene diisocyanate and *m*-dinitrobenzene may act as electron acceptors in the same manner as in the polymerization of a cyclic ether by BPO in the presence of MAH.⁵

**Polymerization of β PL by BPO in the
Presence of Electron Acceptors**

The polymerization of β PL by BPO in the presence of some electron acceptors was investigated (Table X). In the presence of AN or MAH, β PL was effectively polymerized by BPO and the reaction system was colored to deep orange, but in the presence of chloranil or *m*-dinitrobenzene, there was hardly any polymerization. Time-conversion curve for the

TABLE X
Polymerization of β PL by BPO in the Presence of Various Electron Acceptors

β PL, cc	Acceptor, mg	BPO, mg	Conversion, %	Color	
1	Acrylonitrile	10.6	12.1	74 (12) ^a	Orange
1	Maleic anhydride	15.8	12.1	69 (2) ^a	Orange
1	Chloranile	41.0	12.1	1.1 (0.2) ^a	Dark red
1	<i>m</i> -Dinitrobenzene	27.1	12.1	1.0 (1) ^a	Orange

β PL, 1.61×10^{-2} mole; acceptor, 1.61×10^{-4} mole; BPO, 5×10^{-5} mole; at 100°C ; 24 hr; in air.

^a Conversions in brackets are data for the polymerization without BPO catalyst.

polymerization of β PL by BPO in the presence of MAH is shown in Fig. 2. The reaction system remained colorless during the initial 4 hr of reaction and no polymer was produced. After 1 day, the system developed a yellow color and polymerization proceeded.

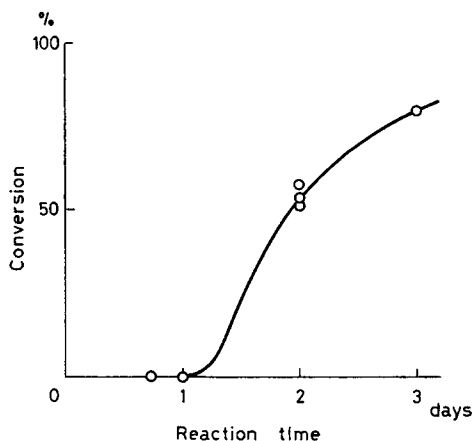


Fig. 2. Polymerization of β PL by BPO in the presence of MAH. β PL, 1 cc; MAH, 1.557 g; BPO, 5×10^{-5} mole; in air; at 60°C .

Graft Copolymerization of β PL onto the Trunk Polymer Containing Ether Groups by BPO in the Presence of MAH

It has been reported⁵ that active species for cationic polymerization of BCMO or TOX were produced by heating with MAH and BPO. However recently,⁹ a conjugated oligomeric radical of MAH has been proposed as an active compound in this polymerization system. In the present work, such polymerization methods were applied to grafting in which the mixture of the trunk polymer containing ether groups, MAH and BPO was heated at 100°C to produce ionic active species (Table XI) and then β PL was added to be graft copolymerized. Graft copolymers were separated from crude products according to the methods shown in Figure 3 and the formation of

TABLE XI
Graft Copolymerization of β PPL onto the Various Trunk Polymers Containing
Ether Groups by BPO in the Presence of MAH as Electron Acceptor

Experi- ment no.	Trunk polymer (doner), g	Preparation of active species				Graft copolymerization				Total conversion %	Grafting efficiency %
		MAH, g	BPO, mg	Temp., °C	Time, min	Color	BPL, cc	Temp, °C	Time, hr		
139-1	PEG(0.5)	0.11	16.1	80	30	Reddish purple	9	80	4	— ^a	—
139-3	POM(0.1)	0.2	16.1	100	20	Black	2	60	20	31.8	—
139-4	St-IBVE copolym. (0.1)	0.2	16.1	100	20	Black	2	60	20	61.0	20.4
139-5	St-DVB-IBVE copolym. (0.1)	0.2	16.1	100	20	Black	2	60	20	24.4	10.3
139-6	P β PL (0.1)	0.2	16.1	100	20	Black	2	60	20	63.4	—

^a Insoluble polymer in cold methanol could be separated, but soluble polymer could not.

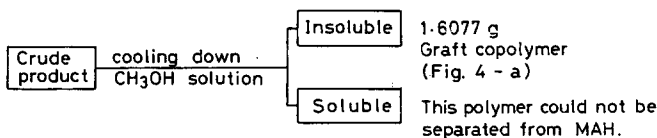
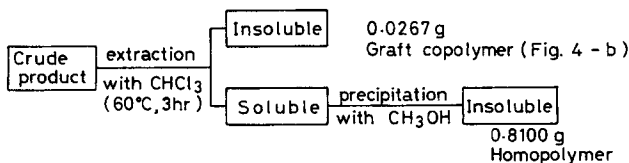
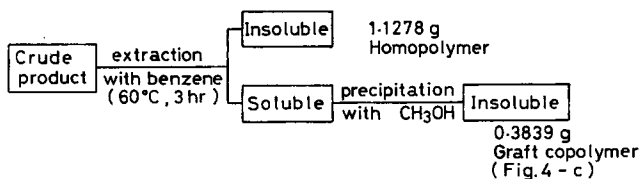
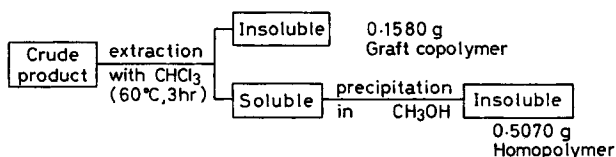
I 39-1 PEG(0.5g) --- MAH--- BPO System + β PL

 I 39-3 POM(0.1g) --- MAH--- BPO System + β PL

 I 39-4 St-IBVE copolymer (0.1g)---MAH---BPO System + β PL

 I 39-5 St-IBVE-DVB copolymer (0.1g)---MAH---BPO System + β PL


Fig. 3. Separation of graft copolymers of β PL onto various trunk polymers containing ether groups.

graft copolymers was confirmed by their infrared spectrum (Fig. 4). In the case of graft copolymerization onto PEG, the polymerization system was colored a reddish purple. This polymer could not be precipitated by the addition of methanol as precipitant. This fact demonstrates the absence of homopolymer ($P\beta$ PL); in other words the grafting efficiency is very high. The methanol solution was cooled down to obtain the precipitate. In the infrared spectrum of the polymer obtained, the characteristic absorptions of $C = O$ (1740 cm^{-1}) and the ether group (1100 cm^{-1}) are observed (Fig. 4a). This high grafting efficiency is due to the frequent chain transfer reaction to the trunk polymer, because the system is homogeneous and cationic growing ends attack easily ether groups on the trunk polymer. In the graft copolymerization of β PL onto POM, the grafting efficiency is very low because the trunk polymer was not dissolved and decomposed easily during the preparation of active species. Also, in the grafting onto St-IBVE copolymer or St-IBVE-DVB copolymer, graft copolymers were produced but the grafting efficiencies are comparably low, 20.0% and 10.3%, respectively, because the

system is heterogeneous. β PL was also used as a trunk polymer and the polymerization of β PL by such initiators shown in Table XI was recognized. The order of the grafting efficiencies toward the trunk polymers is as follows; PEG > St-IBVE copolymer > St-DVB-IBVE copolymer > POM and this order is explained by the following fact. PEG and its graft copolymer are easily dissolved in molten MAH. On the other hand, St-IBVE copolymer is insoluble, but its graft copolymer is soluble. St-DVB-IBVE copolymer and POM are insoluble and POM decomposes during

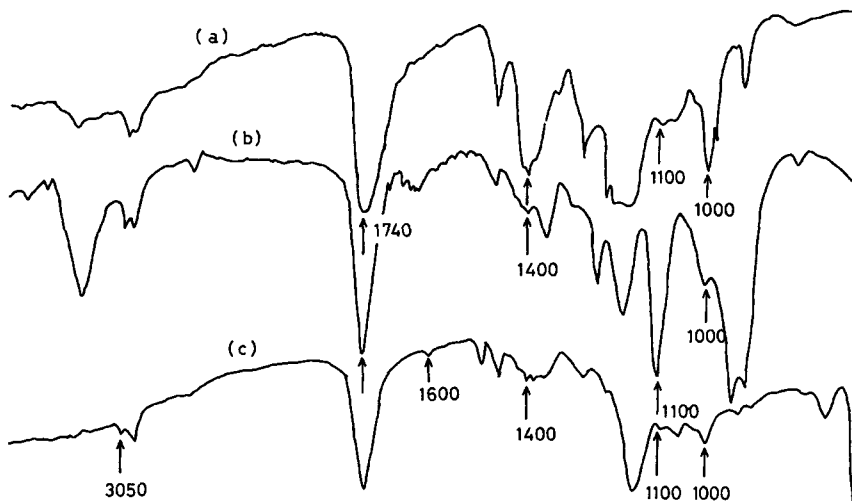


Fig. 4. Infrared spectra of; (A) graft copolymer of β PL onto PEG, (B) graft copolymer of β PL onto POM, (C) graft copolymer of β PL onto St-IBVE copolymer.

preparation of active species. In homogeneous systems, polymeric active species were easily produced in good contact between donor polymer and an acceptor molecule which is thought to be oligomer radical of MAH.⁹

Radiation Induced Graft Copolymerization of β PL onto Electron Donative Trunk Polymers such as PNVCZ or Polymers Containing Ether Groups in the Presence of MAH

In Table XII γ -rays from Co^{60} was used instead of BPO as the initiator. It is well known that NVCZ or *N*-ethyl carbazole forms a donor-acceptor complex with MAH.^{10,11} The mixtures of electron donative trunk polymers (PNVCZ, *N*-ethyl carbazole, PEG or PBCMO) with an electron acceptor (MAH) were preirradiated to produce ionic active species. After that β PL was graft copolymerized (Table XII). Graft copolymers were separated as shown in Figure 5 and confirmed by their infrared spectra. These reaction systems colored deeply. In the case of PNVCZ or *N*-ethyl carbazole,

TABLE XII
Radiation Induced Graft Copolymerization of β PPL onto the Various Electron Donative Trunk Polymers in the Presence of MAH

Experi- ment. no.	Trunk polymer, g	MAH, g	Preirradiation (γ -ray)					Post polymerization				Total conv., %	Color
			Preparation of active species		Total dose, r	Time, Temp., hr °C	β PPL, cc	Time, Temp., hr °C	Product, g	Total conv., %			
			Dose rate, r/hr	Time, Temp., hr °C									
300-1	PNVCZ 0.5	2.5	4.9×10^4	3.3×10^6	68	60	0.5	124	60	0.4988	0	Yellow \rightarrow dark brown	
307-1	PNVCZ 0.5	2.0	—	—	—	—	0.5	124	60	0.4865	0	Yellow	
307-2	EtCZ 0.5	2.0	—	—	—	—	0.5	124	60	0	0	Red	
300-2	PEG 0.5	2.0	4.9×10^4	3.3×10^6	68	60	0.5	124	60	?	?	Red	
300-3	PBCMO 0.5	2.0	4.9×10^4	3.3×10^6	68	60	0.5	124	60	0.6645	32.9	colorless	

^a ? : Insoluble polymer in cold methanol could be separated, but soluble polymer could not.

β PL was not polymerized by this method, but in using PEG or PBCMO β PL was graft copolymerized.

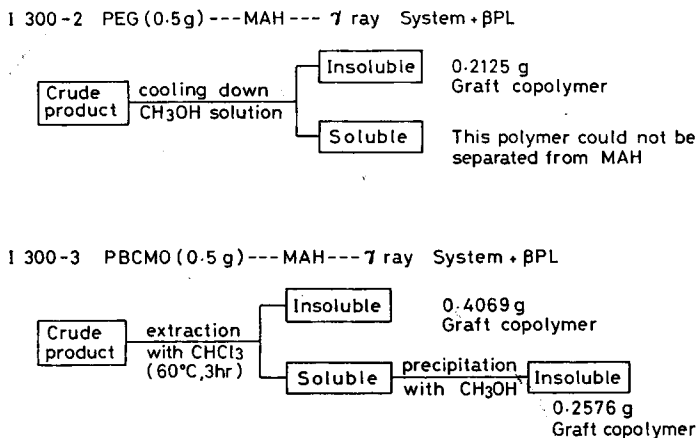


Fig. 5. Separation of graft copolymers of β PL onto various trunk polymers as electron donor in the presence of MAH as electron acceptor.

CONCLUSION

β PL purified by toluene diisocyanate was polymerized by BPO catalyst with the color of deep orange. β PL purified by calcium chloride was not polymerized by BPO in spite of its higher purity, but in the presence of traces of toluene diisocyanate it was polymerized effectively by BPO with the same deep orange color. β PL purified by calcium chloride was not polymerized by irradiation with γ -rays in the liquid state and was also not graft copolymerized onto preirradiated polypropylene. It was not polymerized by BPO or CHP but was polymerized by AIBN. The polymerizations of β PL by BPO in the presence of electron acceptors such as AN, MAH, chloranil or *m*-dinitrobenzene were carried out. This polymerization method was applied to graft copolymerization. A ternary system of the trunk polymer containing ether groups, MAH and BPO was heated and then β PL was added. When the trunk polymer was soluble in molten MAH, the grafting efficiency was very high.

References

1. H. Ohse, H. Cherdron, and F. Korte, *Makromol. Chem.*, **86**, 312 (1965).
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**, 791 (1967).
4. T. Shiota, K. Hayashi, and S. Okamura, *J. Appl. Polym. Sci.*, **12**, 2441 (1968).
5. K. Takakura, K. Hayashi, and S. Okamura, *Annual Report of the Japanese Association for Radiation Research on Polymers*, **5**, 139 (1963-1964); *J. Polym. Sci. A-1*, **4**, 1731 (1966).
6. T. Shiota, Y. Goto, and K. Hayashi, *J. Appl. Polym. Sci.*, **11**, 753 (1967).
7. W. P. Tyler and D. W. Beesing, *Anal. Chem.*, **24**, 1511 (1952).

8. T. L. Gresham, J. E. Jansen, and F. W. Shaver, *J. Am. Chem. Soc.*, **70**, 999 (1948).
9. K. Kondo, Y. Nakayama, K. Hayashi, and S. Okamura, the 17th Annual Meeting of the Society of Polymer Science of Japan, 1968; Abstracts of Papers, p. 89.
10. L. P. Ellinger, *Polym.*, **6**, 549 (1965).
11. L. P. Ellinger, *Polym.*, **6**, 559 (1965).

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