Ionic Graft Copolymerization.

VI. Graft Copolymerization of β-Propiolactone and N-Vinylcarbazole onto Trunk Polymer Containing Carboxylic Acid, Sulfonic Acid, and Their Salts

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Synopsis

It was pointed out in previous papers that both cationic and anionic polymerization might be involved simultaneously in grafting onto trunk polymers containing —COOH or —SO₃Na. The graft copolymerization of β-propiolactone (βPL)–N-vinylcarbazole (NVCZ) onto styrene–divinylbenzene copolymers containing carboxylic acid, sulfonic acid, and their salts was carried out in order to distinguish between the polymers produced by anionic and cationic mechanisms. The polymer obtained by the polymerization of βPL–NVCZ with BF₃·OEt₂, a typical cationic catalyst, consisted mainly of NVCZ units, but the polymer obtained with BuLi, a typical anionic catalyst, consisted mainly of βPL units. In the graft copolymerization of NVCZ–βPL onto trunk polymer containing —COOH, the NVCZ contents of the branch polymer and the toluene-insoluble fraction were estimated to be ca. 50 mole-%; therefore these polymers were produced by both cationic and anionic mechanisms. In the case of graft copolymerization onto the trunk polymer containing SO₃Na, it was found that both cationic and anionic polymerization also occurred simultaneously.

INTRODUCTION

Ionic compounds composed of a pair of ions can be used as cationic, anionic, or relatively neutral catalysts, depending on the nature of the combination of cation and anion.

A series of studies[1,2] has been carried out of the polymerization of β-propiolactone (βPL) by neutral catalyst. It was reported in the previous paper,[1-3] that polymerizations by cationic and anionic mechanisms might coexist in the polymerization of βPL with a neutral catalyst. In this paper the graft copolymerizations of βPL–N-vinylcarbazole (NVCZ) onto trunk polymers containing —COONa, —COOH, —SO₃Na, or —SO₃H are studied. Many attempts to copolymerize βPL with various monomers such as β-lactones,[4] 3,3-bis(chloromethyl)oxetane,[5,6] epichlorohydrin,[7] propylene oxide,[7] acrylonitrile,[8] styrene,[9,10] and ethyleneimine[11] have been made.

NVCZ was used in the present study for the following reasons: *(1)* this monomer is easily polymerized, even by a cationic catalyst of low

activity, such as a relatively neutral salt or weak acid; (*2*)   the composition of polymer produced is easily determined by elementary analysis for nitrogen; (*3*)   the copolymer obtained is a powderlike material and is easily handled.

It is well known that NVCZ polymerizes very easily by a cationic mechanism and βPL polymerizes easily by either a cationic or anionic mechanism. A polymer consisting mainly of NVCZ units is obtained in the copolymerization of βPL and NVCZ by a typical cationic catalyst such as $BF_3 \cdot OEt_2$. On the other hand, a polymer consisting mainly of βPL units is obtained in the copolymerization of βPL and NVCZ by a typical anionic catalyst such as BuLi. Therefore, the polymer obtained by cationic mechanism is possibly separated from the polymer by anionic mechanism. The polymer obtained was separated by the solvent extraction to a toluene-soluble fraction (F_{PNVCZ}), a chloroform-soluble fraction ($F_{P\beta PL}$), and an insoluble fraction of grafted material (F_G). The polymerization mechanisms were investigated by the determination of the compositions of these polymer fractions. In the graft copolymerization of βPL and NVCZ onto trunk polymer containing carboxyl group (RCOOH) as a relatively covalent neutral catalyst, the cationic polymerization of NVCZ by H^+ and the anionic polymerization of βPL by $RCOO^-$ occur simultaneously in the same reaction system. Also, in the graft copolymerization onto trunk polymer containing sodium sulfonate (RSO_3Na) as a ionic neutral catalyst, both cationic and anionic polymerization occur simultaneously.

EXPERIMENTAL

Reagents

βPL was purified by $CaCl_2$ as shown in a previous paper.[12]   NVCZ was recrystallized three times from purified *n*-hexane solution. The various trunk polymers used were prepared by the same methods as described in our previous paper.[2]

Procedure of Graft Copolymerization

Toluene solution of βPL and NVCZ was added onto 100–200 mesh powder of dried trunk polymer and then was polymerized *in vacuo* at 60°C under polymerization conditions shown in Table I. In the case of
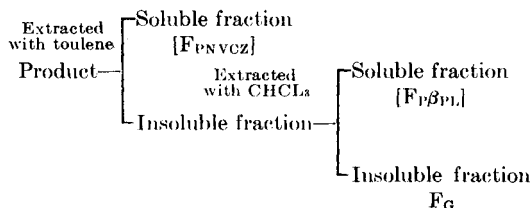

Fig. 1. Fractionation of graft copolymer of βPL–NVCZ onto trunk polymer (St–DVB copolymer).

TABLE I. Reaction Conditions of Graft Copolymerization of βPL and NVCZ

No.	NVCZ			βPL			Total		Solvent (toluene), cc	Trunk polymer, g	Catalyst, mole
	NVCZ + βPL	mole ×10⁻²	g	mole ×10²	g	cc	mole	g			
0	1	0.777	1.500	0	0	0	0.777×10^{-2}	1.500	6.0	0.150	6.6×10^{-4}
1	0.467	1.127	2.180	1.288	0.926	0.8	2.415×10^{-2}	3.106	4.5	"	"
2	0.333	0.805	1.555	1.61	1.158	1.0	"	2.713	4.9	"	"
3	0.200	0.482	0.932	1.933	1.390	1.2	"	2.322	5.4	"	"
4	0.133	0.320	0.618	2.095	1.506	1.3	"	2.124	5.6	"	"
5	0.066	0.160	0.309	2.255	1.621	1.4	"	1.930	5.8	"	"
6	0.034	0.081	0.1565	2.334	1.680	1.45	"	1.837	5.9	"	"
7	0	0	0	2.415	1.737	1.5	"	1.737	6.0	"	"

TABLE II
Thermal Polymerization of βPL–NVCZ[a]

Expt no.	Polymerization system	Toluene, cc	Temp, °C	Time, hr	Conversion, %	Grafting, %	Grafting efficiency, %
G15-1	NVCZ + βPL[b]	4	60	120	0.66	—	—
G15-2	"	4	60	240	0.70	—	—
G15-4	"	4	80	48	trace	—	—
G15-3	"	4	120	3	0.36	—	—
G25-1	St–DVB copolymer + NVCZ + βPL[c]	5.6	80	48	1.84	3.73	14.3

[a] NVCZ in monomer mixture 20 mole-%.
[b] NVCZ, 0.5 g; βPL, 0.579 g.
[c] St–DVB copolymer, 0.15 g; NVCZ, 0.618 g; βPL, 1.505 g.

cationic catalyst, such as $BF_3 \cdot OEt_2$ or RSO_3H, copolymerization was carried out at $0°C$ in nitrogen because of the high polymerization reactivity even at room temperature.

Separation of Graft Copolymer

PNVCZ dissolves in toluene, P-βPL does not dissolve in toluene but dissolves in chloroform, and the graft copolymer is insoluble in both, because of crosslinking of the trunk polymer. The crude product was separated into three fractions by the solvent extraction as shown in Figure 1.

Measurement of Intrinsic Viscosity

The intrinsic viscosity of the polymer mainly consisting of βPL units was measured at $35°C$ in chloroform solution and that of the polymer mainly consisting of NVCZ units was measured at $25°C$ in benzene.

RESULTS

Polymerization of βPL–NVCZ without Catalyst

βPL and NVCZ might be polymerized without catalyst for the following reasons: (1) existence of anionic polymerization of βPL initiated by the high basicity of NVCZ; (2) occurrence of spontaneous polymerization of βPL; (3) occurrence of radical polymerization of NVCZ; (4) strong electron-donor character[13-15] of NVCZ. NVCZ might be polymerized through an electron donor–acceptor complex by some compounds such as toluene and the divinylbenzene units and styrene units in the reaction system. βPL and NVCZ were polymerized in toluene in the presence of St–DVB copolymer without catalyst under the same conditions as graft copolymerization. Such a secondary reaction can be eliminated under the grafting conditions, considering the very much lower conversion of the polymerization without catalyst relative to that of the grafting, as shown in Table II.

Copolymerization of βPL–NVCZ by $BF_3 \cdot OEt_2$

βPL and NVCZ were copolymerized by $BF_3 \cdot OEt_2$ as a typical cationic catalyst under milder conditions than the other copolymerization runs, and then the reaction mixture was poured into an excess of ammoniacal methanol in order to stop the reaction and isolate the polymer produced (Table III). The rate of copolymerization increased with increasing NVCZ content in the monomer mixture. These results show that NVCZ has higher polymerization activity by a cationic mechanism than βPL. Only a toluene-soluble fraction was obtained with the typical cationic catalyst. The compositions of polymers were determined from their nitrogen contents. The NVCZ content of polymer obtained was determined to be 88–95 mole-%; the copolymer consists of mainly NVCZ units.

TABLE III
Copolymerization of βPL–NVCZ by $BF_3 \cdot OEt_2$[a]

			Fractionation, g			Analysis
$\dfrac{NVCZ}{NVCZ + \beta PL}$	Time, min	Con- version, %	F_{PNVCZ}	$F_{P\beta PL}$	N, %	NVCZ content in polymer, %
0.466	6	23.3	0.7253	0	7.1	95.2
0.333	6	13.4	0.3618	0	7.1	95.2
0.20	8	2.1	0.0485	0	7.0	91.3
0.133	9	17.8	0.3780	0	7.0	91.3
0.066	15	10.6	0.2052	0	6.9	88.2

[a] $BF_3 \cdot OEt_2$, 6.6×10^{-7} mole; monomer mixture, 2.42×10^{-2} mole; total volume, 7.5 cc; in toluene, in nitrogen, 0°C.

Copolymerization of βPL–NVCZ by BuLi

The βPL and NVCZ monomer mixture was copolymerized by BuLi as a typical anionic catalyst (Table IV). Crude polymer was separated to $F_{P\beta PL}$ and a small amount of F_{PNVCZ}. $F_{P\beta PL}$ consists of only βPL units. Therefore, in the polymerization of βPL and NVCZ by the anionic mechanism, the polymer obtained consists of mainly βPL units.

On the other hand, the polymer obtained in cationic polymerization consists mainly of NVCZ units (Table III).

Graft Copolymerization of βPL–NVCZ onto Trunk Polymer Containing SO_3H

The results of graft copolymerization of βPL–NVCZ onto the trunk polymer containing SO_3H are summarized in Table V. βPL is hardly polymerized under such mild conditions (0°C, for 5 min), but the rate of polymerization onto RSO_3H increases with increasing NVCZ content in the monomer. The grafting efficiency is very low (1–5%). A large amount of toluene-soluble fraction (F_{PNVCZ}) and a trace of graft polymer (F_G) were obtained. The toluene-soluble fraction consists mainly of NVCZ units.

Graft Copolymerization of βPL–NVCZ onto Trunk Polymer Containing SO_3Na

The relationships of total conversion, per cent grafting, and grafting efficiency against NVCZ content in the monomer mixture are shown in Figure 2. The total conversion increases but the per cent grafting and the grafting efficiency tend to decrease with increasing NVCZ content in the monomer because of the increase in cationic polymerizability. The crude polymer was separated into three fractions by the methods shown in Figure 1. The conversions and the polymer compositions of each polymer fraction are shown in Figure 3. The conversion of F_{PNVCZ} increases and

TABLE IV
Copolymerization of βPL–NVCZ by BuLi[a]

Expt. no.	$\dfrac{\text{NVCZ}}{\text{NVCZ} + \beta\text{PL}}$, mole-%	Time, min	Conversion, %	Fractionation, g		NVCZ content in polymer, mole-%	
				F_{PNVCZ}	$F_{P\beta PL}$	F_{PNVCZ}	$F_{P\beta PL}$
G79-0	100	10	0.65	0.0097	—	100	—
G79-12	33.3	2	9.4	0.0049	0.2508	—	~0
G79-13	20.0	2	13.1	0.0020	0.3035	—	~0
G79-14	13.3	2	14.9	0.0020	0.3152	—	~0
G79-7	0	10	53.9	—	0.9373	—	0

[a] Monomer mixture, 2.42×10^{-2} mole; BuLi, 6.6×10^{-4} mole; in toluene; total volume, 7.5 cc; 30°C, in N_2.

TABLE V
Graft Copolymerization of βPL–NVCZ onto Trunk Polymer Containing SO_3H[a]

Expt. no.	NVCZ NVCZ + βPL, mole-%	Time, min	Total conversion, %	Grafting, %	Grafting efficiency, %	Branching polymer, g	Fractionation Toluene-soluble fraction, g (mole-% NVCZ)	$CHCl_3$-soluble fraction, g
G71-1	100	5	93.8	1.5	0.16	0.0015	0.9371 (100)	0
G71-2	33	1	8.0	3.3	2.3	0.0033	0.1416 (98.5)	0
G72-3	20	1	6.2	2.6	2.7	0.0026	0.0936 (97.3)	0
G23-4	6.6	2	10.8	4.7	3.4	0.0047	0.1351 (92.3)	0
G23-5	3.3	3	7.1	3.1	3.5	0.0031	0.0838 (83.5)	0
G23-6	0	5	0.1	~0	—	~0	0	0.0010

[a] Trunk polymer, 100 mg; —SO_3H, 4.4×10^{-4} mole; monomer mixture, 1.61×10^{-2} mole; total volume, 5 cc; in toluene, in N_2; 0°C.
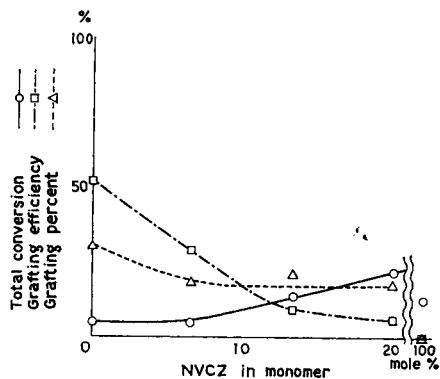
Fig. 2. Graft copolymerization of NVCZ–βPL onto trunk polymer containing SO₃Na. Trunk polymer, 100 mg; SO₃Na content, 4.5×10^{-4} mole; monomer mixture, 1.61×10^{-1} mole; total volume, 5 cc; in toluene; in N_2; 60°C; 258 hr.
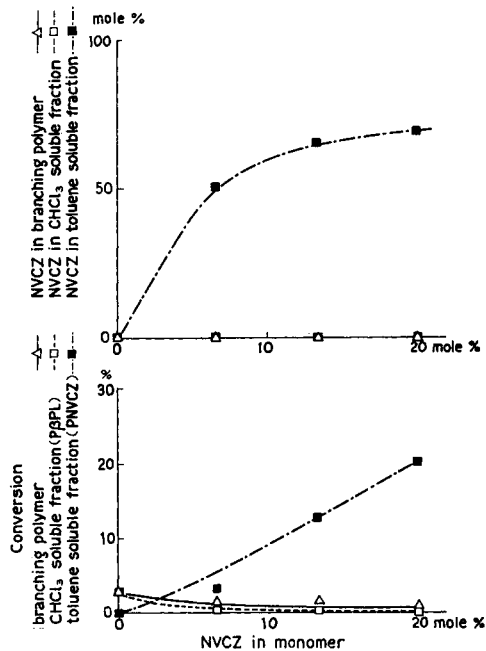

Fig. 3. Fractionation of the graft copolymer of NVCZ–βPL onto trunk polymer containing SO₃Na.

the conversions of F_G and $F_{PβPL}$ decrease with increase of NVCZ content in monomer. Polymer fractions F_G and $F_{PβPL}$ consist mainly of βPL units and F_{PNVCZ} has a composition intermediate between the polymers obtained by anionic and cationic mechanism. Therefore, these results demonstrate that F_G and $F_{PβPL}$ were produced by an anionic mechanism and F_{PNVCZ} was produced by both anionic and cationic mechanism.

Graft Copolymerization of βPL and NVCZ onto Trunk Polymer Containing COOH

βPL and NVCZ were graft copolymerized onto the trunk polymer containing COOH at 80°C for 2 days. NVCZ and βPL hardly polymerize
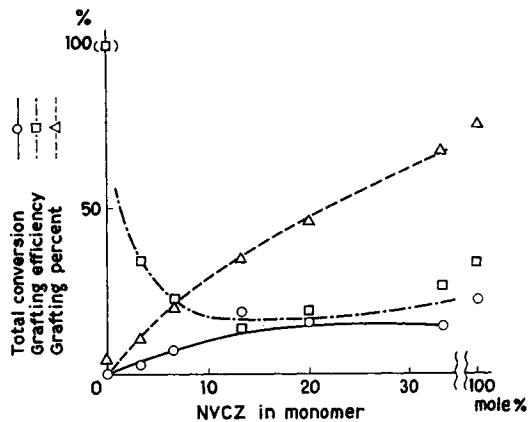

Fig. 4. Graft copolymerization of NVCA–βPL onto trunk polymer containing COOH. Trunk polymer, 100 mg; COOH content, 4.5×10^{-4} mole; monomer mixture, 1.61×10^{-4} mole; total volume, 5 cc; in toluene; 80°C; 2 days.
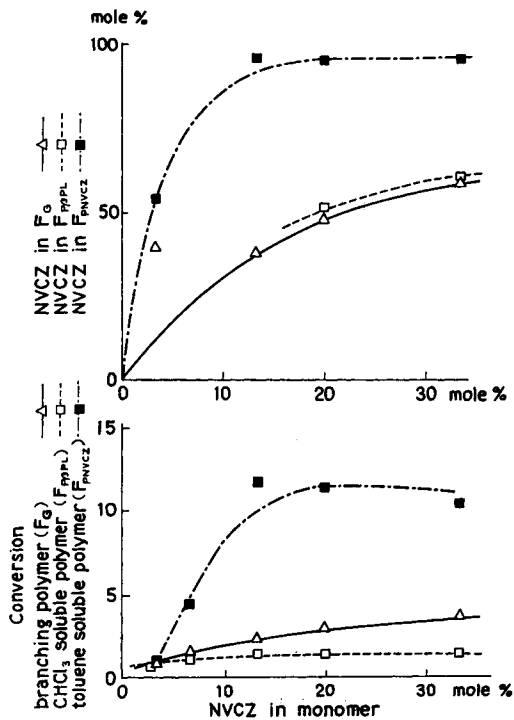

Fig. 5. Fractionation of the graft copolymer of NVCZ–βPL onto trunk polymer containing COOH.

without catalyst, even under such severe conditions (Table II, G15-4). Plots of the total conversion, the per cent grafting and the grafting efficiency against monomer composition are shown in Figure 4. Total conversion and per cent grafting increase with NVCZ content in the monomer, but grafting efficiency decreases. The crude polymer was separated into three fraction as shown in Figure 1. The conversions and the composition of F_{PNVCZ}, $F_{P\beta PL}$, and F_G are shown in Figure 5. The composition of F_{PNVCZ}, which is the main product, corresponds which that of polymer obtained by cationic mechanism. F_G and $F_{P\beta PL}$ have compositions intermediate between the polymers obtained by anionic and cationic mechanisms, therefore, it is presumed that these polymers are produced by both cationic and anionic mechanisms. NVCZ which is not polymerized by an anionic mechanism is unexpectedly contained in the branch polymer produced by an anionic mechanism. Such an unexpected result is attributed to the termination reaction between growing cation of PNVCZ and COO^- in the trunk polymer as shown in Table VI.

Graft Copolymerization of βPL and NVCZ onto Trunk Polymer Containing COONa

Graft copolymerization of βPL and NVCZ onto the trunk polymer containing COONa as anionic initiator was carried out. Total conversion, per cent grafting, and grafting efficiency decrease with increasing NVCZ content in the monomer (Fig. 6). These results indicate that polymerization by COONa proceeds by an anionic mechanism. The crude product was separated into three fractions. Conversions of F_G and $F_{P\beta PL}$ decrease but that of F_{PNVCZ} increases with increasing NVCZ content in the monomer mixture (Fig. 7). Therefore the decrease of grafting efficiency is attributed to production of F_{PNVCZ}.
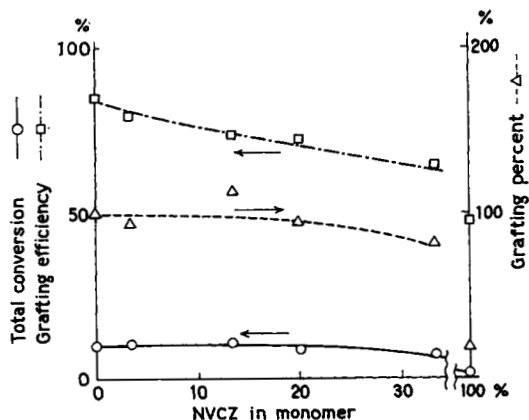

Fig. 6. Graft copolymerization of NVCZ–βPL onto trunk polymer containing COONa Trunk polymer, 100 mg; COONa in trunk polymer, 4.4×10^{-4} mole; monomer mixture, 1.61×10^{-2} mole; total volume, 5 cc; in toluene; in N_2; 60°C; 5 hr.
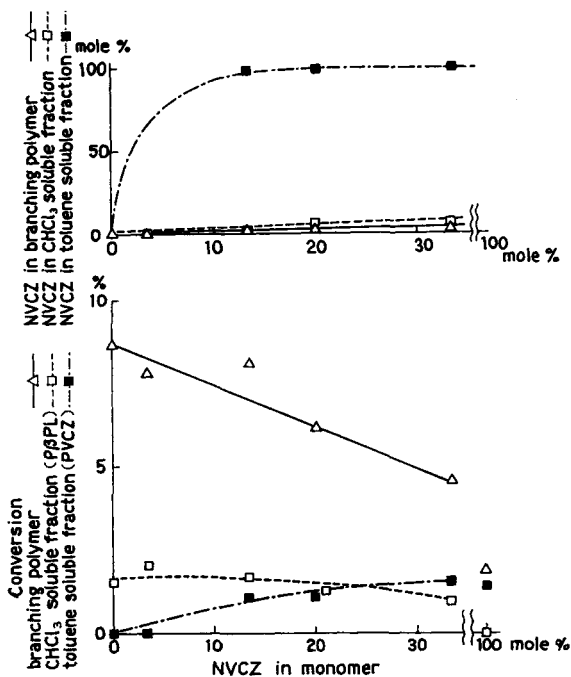
Fig. 7. Fractionation of graft copolymer of NVCZ–βPL onto trunk polymer containing COONa.

The composition of each polymer fraction is shown in Figure 7. F_G and $F_{P\beta PL}$ are the polymers obtained by an anionic mechanism and F_{PNVCZ} is the polymer obtained by cationic mechanisms.

Comparison of Graft Copolymerization of βPL and NVCZ onto Various Trunk Polymers

The graft copolymerization of βPL and NVCZ onto the various trunk polymers was compared with the copolymerization of βPL and NVCZ by a typical cationic catalyst and a typical anionic catalyst (Fig. 8). The rate of copolymerization decreases in the order $BF_3OEt_2 >$ —$SO_3H >$ BuLi $>$ —COONa $>$ —COOH $>$ —SO_3Na. On the other hand, grafting efficiency increases gradually to the trunk polymer containing anionic catalyst from the trunk polymer containing cationic catalyst. A large amount of F_{PNCvz} is produced in the cationic copolymerization of βPL and NVCZ, and the copolymer consists mainly of NVCZ units. In the anionic copolymerization of βPL and NVCZ, however, a large amount of $F_{P\beta PL}$ is produced and the copolymer consists mainly of βPL units. It was concluded from the polymer compositions that the trunk polymer containing —SO_3H initiates cationic polymerization and the trunk polymer containing —COONa initiates anionic polymerization, but the trunk polymers containing

—COOH or —SO₃Na simultaneously initiate both cationic and anionic polymerization.

Copolymer compositions of total polymer produced by various trunk polymer are plotted against monomer composition (Fig. 9). The order of cationic polymerization activity is $BF_3OEt_2 \approx SO_3H > —COOH > —SO_3Na > —COONa > BuLi$.
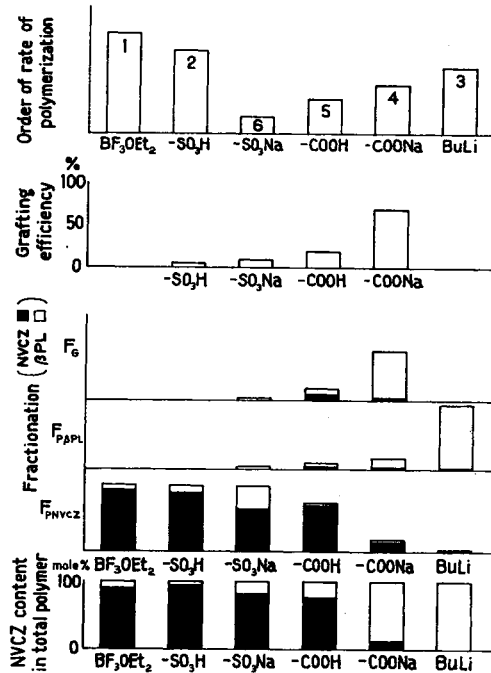
Fig. 8. Summary of the graft copolymerization of βPL–NVCZ onto various trunk polymers. NVCZ in monomer, 20 mole-%.

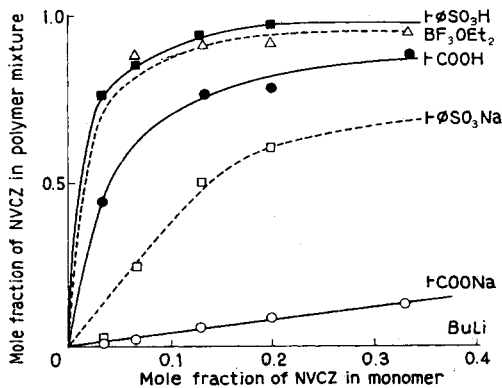Fig. 9. Copolymer composition curves for graft copolymerization of NVCZ–βPL onto various trunk polymers.

Graft Copolymerization by Means of Chain Termination Reaction of Growing Cation onto COO⁻ in Trunk Polymer

Although NVCZ is not polymerized by an anionic mechanism, a large amount of NVCZ is contained in the branch polymer which is produced by an anionic mechanism. This unexpected result is elucidated by considering the chain termination of the PNVCZ growing cation with COO⁻ in the trunk polymer. Then, NVCZ or βPL was polymerized by cationic catalyst in the presence of the trunk polymer containing —COOH or —COONa. The graft copolymer was obtained as shown in Table VI but, grafting efficiency is very low.

Comparison between Graft Copolymerization of βPL and NVCZ onto —SO₃Na Trunk Polymer in Bulk and in Toluene

It was presumed in our previous paper[1,2] that the mechanism of initiation by the addition product of βPL and —SO₃Na predominates in the polymerization in toluene, but the mechanism of initiation by cation exchange between —SO₃Na and acrylic acid predominates in bulk polymerization.

Graft copolymerization in bulk and in toluene of βPL and NVCZ onto —SO₃Na trunk polymer was also compared (Table VII). In the graft copolymerization of βPL of NVCZ onto —SO₃Na trunk polymer in bulk, the grafting efficiency is very low (1.68%), and the polymer produced by cationic mechanism (NVCZ content of F_{PNVCZ}, 91.6 mole-%) and the polymer produced by anionic mechanism (NVCZ content of $F_{PβPL}$, ~0 mole-%) are obtained as separate fractions. On the other hand, in the graft
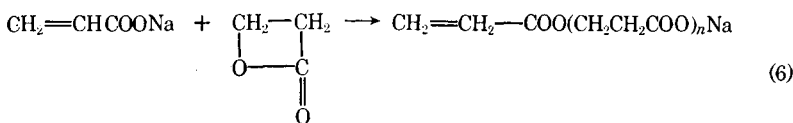
$$RSO_3Na + \underset{\underset{O-C=O}{|\quad\quad|}}{CH_2-CH_2} \longrightarrow RSO_3CH_2CH_2COONa \tag{1}$$

$$RSO_3CH_2CH_2COONa + βPL + NVCZ \longrightarrow$$

$$RSO_3^{\ominus\oplus} \underset{N}{(CH-CH_2)_n}-CH_2CH_2COO(CH_2CH_2COO)_m^{\ominus}Na^{\oplus} \tag{2}$$

$$RSO_3H + CH=CH-----(CH-CH_2)_{n-1}-CH_2CH_2COO(CH_2CH_2COO)_mNa \tag{3}$$

block polymer

$$RSO_3Na + CH_2=CHCOOH \rightleftarrows RSO_3H + CH_2=CHCOONa \tag{4}$$

$$RSO_3H + NVCZ \longrightarrow RSO_3^{\ominus\oplus}(HC-CH_2)_n-H \tag{5}$$

$$CH_2=CHCOONa + \underset{\underset{O-C}{|\quad\,|}}{CH_2-CH_2} \longrightarrow CH_2=CH_2-COO(CH_2CH_2COO)_nNa \tag{6}$$
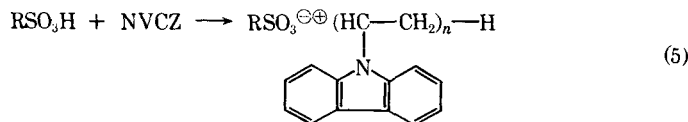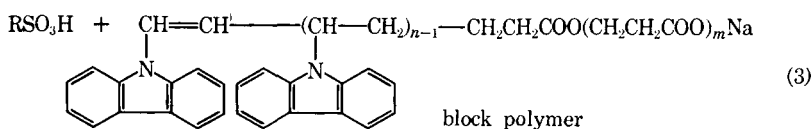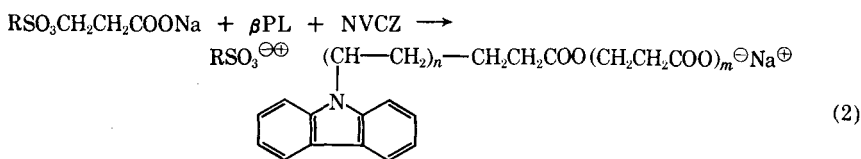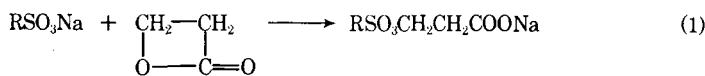
TABLE VI

Graft Copolymerization by Means of Chain Termination of Growing Cation onto COO⁻ in Trunk Polymer[a]

Expt no.	Trunk polymer and wt, g	β-PL, cc	NVCZ, g	Toluene, cc	$CH_3\phi SO_3H$, mole	Time, hr	Conversion, %	Grafting, %	Grafting efficiency, %
G51-1	ST–DVB–AA, 0.15	1.5	—	6	6.6×10^{-5}	3	50.5	7.1	1.21
G51-2	ST–DVB–AA, 0.05	—	0.5	2	"	1	30.0	20.0	6.67
G51-3	ST–DVB–ANa, 0.1257	1.5	—	6	"	3	54.3	35.3	4.71
G51-4	ST–DVB–ANa, 0.05	—	0.5	2	2.2×10^{-5}	1	27.2	15.4	5.65

[a] COO⁻ in trunk polymer, 6.6×10^{-4} mole/150 mg; in N_2; 60°C.

TABLE VII

Graft Copolymerization of NVCZ–βPL onto Trunk Polymer containing SO_3Na in Bulk and in Toluene[a]

Exp. no.	Trunk polymer	Reaction system	Time, hr	Total conversion, %	Grafting, %	Grafting efficiency, %	Fractionation, g (and NVCZ in polymer, mole-%)		
							F_G[b]	F_{PNVCZ}	$F_{P\beta PL}$
G76-1	—SO₃Na	Bulk	6	10.1	0.53	1.68	0.0008 (—)	0.0248 (91.6)	0.0221 (~0)
G22-4	—SO₃Na	In toluene (5.8 cc)	258	5.1	19.2	29.1	0.0288 (~0)	0.0618 (51.5)	0.082 (~0)
G76-2	—SO₃Na + AA (6.6 × 10⁻⁴ mole)	"	200	6.4	~0	~0	0 (—)	0.1125 (91.3)	0.0132 (~0)

[a] Trunk polymer, 0.150 g; —SO₃Na in trunk polymer, 6.6×10^{-4} mole; NVCZ, 0.309 g; βPL, 1.621 g; NVCZ/NVCZ + βPL, 6.6 mole-%; 60°C; in N_2.
[b] Branch polymer.

TABLE VIII

Intrinsic Viscosity of F_PVCZ (Toluene-Soluble Fraction) Obtained in Graft Copolymerization of NVCZ–βPL onto the Various Trunk Polymers

Expt. no.	Catalyst	NVCZ in polymer, mole-%	F_PVCZ		F_PβPL			
			NVCZ in polymer, mole-%	$[\eta]$[a]	NVCZ in polymer, mole-%	$[\eta]$[a]	$\overline{DP}$	$\overline{M}_n$
G21-2	BF₃OEt₂	0.33	95.2	0.5	—	—	—	—
G23-2	—φSO₃H	0.20	~100	0.17	—	—	—	—
G22-1	—φSO₃Na	0.33	34.1	0.125	0	0.475	328	23600
G25-1	—COOH	0.33	96.2	0.21	—	—	—	—
G24-1	—COONa	0.33	~100	0.33	6.32	0.16	74.0	5330
—	NEtCZᵇ	—	100	0.014	—	—	—	—

[a] In benzene at 25°C.
[b] N-Ethylcarbazole.

copyrimerization in toluene, the grafting efficiency is comparatively high (29.1%), and there is a polymer fraction (F_{PNVCZ}) produced by both of cationic and anionic mechanism (NVCZ content of F_{PNVCZ}, 51.5 mole-%). These results demonstrate that the mechanism shown by eqs. (1)–(3) predominates in the graft copolymerization in toluene, but the mechanism shown by eqs. (4)–(6) predominates in bulk.

When equivalent acrylic acid was added in the graft copolymerization system in toluene, the same behavior as in bulk was observed (Table VII, G 76-2). This result supports the mechanism shown by eqs. (4)–(6) for the graft copolymerization of βPL and NVCZ onto —SO_3Na trunk polymer in bulk.

Intrinsic Viscosity of $F_{P\beta PL}$ and F_{PNVCZ} Obtained in the Graft Copolymerization onto Various Trunk Polymers

It was found that both a polymer produced by anionic mechanism and a polymer produced by cationic mechanism are obtained in the polymerization of βPL and NVCZ by a neutral catalyst. Intrinsic viscosities of these fractions were measured (Table VIII). Intrinsic viscosities of the polymer fractions (F_{PNVCZ}) obtained in the grafting onto various trunk polymers are very much larger than that of N-ethylcarbazole, therefore these fractions are polymers.

DISCUSSION

Proposed Mechanism of Polymerization by Sodium Sulfonate

The polymerization behaviors of βPL by sodium sulfonate which has been investigated in this paper and our previous paper[1,2] is summarized as follows.

Homopolymerization of βPL. The rate of polymerization by CH_3-ϕSO_3Na in bulk is quite fast but that in toluene is very slow.

βPL is converted easily into acrylic acid by heating in bulk, but it is almost never converted in toluene.

The rate of polymerization of βPL by $CH_3\phi SO_3Na$ in toluene is accelerated by addition of acrylic acid.

The polymer obtained by $CH_3\phi SO_3Na$ has a double bond at one end and a carboxyl group at another end.

Graft Copolymerization of βPL. Grafting efficiency is lower than that in the grafting onto trunk polymer containing anionic catalyst (—COONa), but is a little higher than that in grafting onto the trunk polymer containing catalyst (—SO_3H).

Grafting efficiency in bulk is very much lower than that in toluene.

βPL is polymerized only on the surface of trunk polymer. The homopolymer by-product is produced in low amounts because of the low polymerization activity.

Graft Copolymerization of βPL and NVCZ. The rate of polymerization increases, but per cent grafting and grafting efficiency decrease with increasing NVCZ content in monomer.

F_G and $F_{P\beta PL}$ consist of only βPL units, but F_{PNVCZ} has a composition intermediate between the polymers obtained by cationic and anionic mechanisms. These results demonstrate that the initiation mechanism shown by eq. (1) predominates in the polymerization in bulk and that shown by eq. (4) predominates in toluene.

When βPL and NVCZ are polymerized by sodium sulfonate, both anionic and cationic polymerizations occur simultaneously in the same reaction system.

Proposed Mechanisms of Polymerization by Carboxylic Acid

Two polymerization mechanisms, namely cationic polymerization initiated by a proton and anionic polymerization initiated by a carboxyl anion, are proposed for the polymerization by carboxylic acid.

The results on polymerization behavior of βPL with carboxylic acid[1,2] are summarized as follows.

For polymer obtained with acetic acid, about 50% of polymers have acetyl groups and carboxyl groups at each polymer chain end. In addition, the other 50% of polymers have double bonds and carboxyl groups.

The characteristic bands corresponding to acid anhydride, which must be observed in the polymer produced in cationic mechanism, could not be detected in the infrared spectrum of low molecular weight polymer obtained by acetic acid.

The grafting efficiency is relatively higher than in the case of trunk polymers containing cationic or ionic neutral catalyst, but lower than in those with anionic catalyst.

In the graft copolymerization of βPL and NVCZ, both cationic and anionic polymerization occur simultaneously.

In the graft copolymerization onto RCOOH trunk polymer, it was expected that graft copolymer might be produced by the termination reaction of growing cations initiated by the proton with carboxyl anion in the trunk polymer (Table VI). The grafting efficiency in the graft copolymerization by chain termination between the growing cation and the carboxyl anion in the trunk polymer is very low, but the grafting efficiency onto the trunk polymer containing —COOH was relatively high.

These results demonstrate that the polymerization of βPL by carboxylic acid proceeds predominantly by the anionic mechanism, and the copolymerization of βPL and NVCZ by carboxylic acid proceeds simultaneously by both anionic and cationic mechanisms.

CONCLUSION

Initiation mechanisms of ionic neutral and covalent neutral catalysts were investigated by means of graft copolymerization of βPL and NVCZ.

The order of the rate of polymerization and the grafting efficiency are $SO_3H > COONa > COOH > SO_3Na$ and $COONa > COOH > SO_3Na > SO_3H$.

Since the polymers obtained by the cationic and anionic mechanism consist of mainly NVCZ and βPL, respectively, they could be separated conveniently.

In the graft copolymerization of βPL and NVCZ onto SO_3Na trunk polymer, small amount of F_G and $F_{P\beta PL}$ consist mainly of βPL units, which F_{PNVCZ} has a composition intermediate between the polymers obtained by anionic and cationic mechanisms.

Therefore, it was concluded that F_G and $F_{P\beta PL}$ are produced by an anionic mechanism and F_{PNVCZ} is produced by both anionic and cationic mechanisms.

Also, simultaneous polymerization by cationic and anionic mechanisms was observed in the grafting onto the trunk polymer containing COOH.

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