

## *Simultaneous Polymerization by Cationic and Anionic Catalysts\**

By

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In our previous paper simultaneous cationic and anionic polymerizations have been reported to proceed in the case of the graft copolymerization of  $\beta$ -propiolactone with N-vinyl carbazole onto the trunk polymers containing  $-\text{SO}_3\text{Na}$  or  $-\text{COOH}$  groups.

In this paper, the simultaneous polymerization by cationic and anionic catalysts was carried out in a liquid system for homopolymerization. The cationic and anionic polymerizations were recognized to occur simultaneously at the comparative rates of both cationic and anionic polymerizations, at least in the case having one of the following conditions at;

- (i) relatively heterogeneous system.
- (ii) the reaction medium having high dielectric constant, or
- (iii) relatively stable growing anionic and cationic ends.

### **Introduction**

In the previous paper<sup>1)</sup>, it has been reported that both cationic and anionic polymerizations possibly coexist in the graft copolymerization of  $\beta$ -propiolactone ( $\beta$ PL) and N-vinyl carbazole (NVCZ) onto the trunk polymers containing  $-\text{COOH}$  or  $-\text{SO}_3\text{Na}$  groups. A few examples of simultaneous polymerizations of both cationic and anionic mechanisms have been reported. It was confirmed, for example, by Kambara *et al.*<sup>2)</sup> that in the copolymerization of styrene with isoprene initiated by Ziegler-type catalyst, two kinds of polymers were obtained in which one was a high molecular weight polymer consisting mainly of cis 1,4 isoprene units obtained by cationic mechanism and another was a low molecular weight polymer consisting mainly of trans 1,4 isoprene units obtained by coordinated anionic mechanism. It was demonstrated also by Saegusa *et al.*<sup>3,4)</sup> that there were two kinds of active sites from which a coordinated anionic polymerization and a cationic polymerization could start in the polymerization of alkylene oxide<sup>3)</sup> or the copolymerization of epichlorhydrine with tetrahydrofuran<sup>4)</sup> initiated by  $\text{Al}(\text{C}_2\text{H}_5)_3\text{-H}_2\text{O}$  or  $\text{Al}(\text{C}_2\text{H}_5)_3$  catalysts. Also in the study of copolymerization of vinylidene cyanide

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with vinyl ether by radical catalyst<sup>5</sup>), a rapid ionic polymerization precluded the free radical initiation so that both cationic and anionic polymerizations occurred simultaneously in which vinyl ether acted as a base toward vinylidene cyanide while vinylidene cyanide acted as an acid toward vinyl ether.

In this paper, simultaneous polymerizations of  $\beta$ PL and NVCZ by both cationic and anionic catalysts are carried out and the possible conditions of simultaneous polymerization are investigated.

Supposingly when cationic and anionic living ends may combine together during the polymerization, the polymerization shall be terminated to form a block copolymer. The synthesis of block copolymer by the reaction of cationic living polymer ends with anionic living polymer both prepared in separate vessels has been reported by Berger *et al.*<sup>6</sup>) and Asami *et al.*<sup>7</sup>). Their methods are convenient only for the case of the propagating cation and anion having enough long life times, while the method described in this paper may be able to be used even in the cases of propagating ends having relatively short life time.

## Experimental

### Reagents

$\beta$ PL<sup>8</sup>) and NVCZ<sup>1</sup>) are purified by the same methods as mentioned in the previous papers. Toluene, nitrobenzene, dichloroethane and dioxane are purified by the usual procedures.

### Polymerization

Three polymerization methods are adopted to prevent the direct neutralization reaction between cationic and anionic catalysts.

#### (1) Simultaneous polymerization in the heterogeneous system

The mixture of various ratios of  $\beta$ PL and NVCZ are added onto solid catalyst mixture of cationic and anionic species (for example, *p*-toluene sulfonic acid and sodium acetate).

#### (2) Simultaneous polymerization in homogeneous system

Monomer mixtures of  $\beta$ PL and NVCZ are first polymerized by sodium acetate, and then *p*-toluene sulfonic acid-solution is added into this reaction system for further cationic polymerization.

#### (3) Cationic polymerization in the presence of anionic catalyst

The cationic polymerizable monomer such as NVCZ, isobutyl vinyl ether (iBVE),  $\alpha$ -methylstyrene ( $\alpha$ -MeSt) or trioxane (TOX) is polymerized by cationic catalyst with the presence of slightly excess amount of equivalent anionic catalyst.

### Fractionation of the block copolymer

Procedures for the fractionation of the block copolymer are shown in Fig. 1. A crude polymer is dissolved in chloroform and the first polymer fraction ( $F_{P\beta PL}$ ) is separated by adding of toluene (8 times in volume of chloroform solution). And then acetic acid (8 times in volume of toluene solution) is added to the above mentioned toluene solution, in the precipitation of which the second polymer fraction  $F_{PNVCZ}$  mainly consisted of NVCZ, is isolated as shown in Fig. 1. The remaining fraction, soluble in either of toluene and acetic acid, seems to be a copolymer (probably block copolymer).

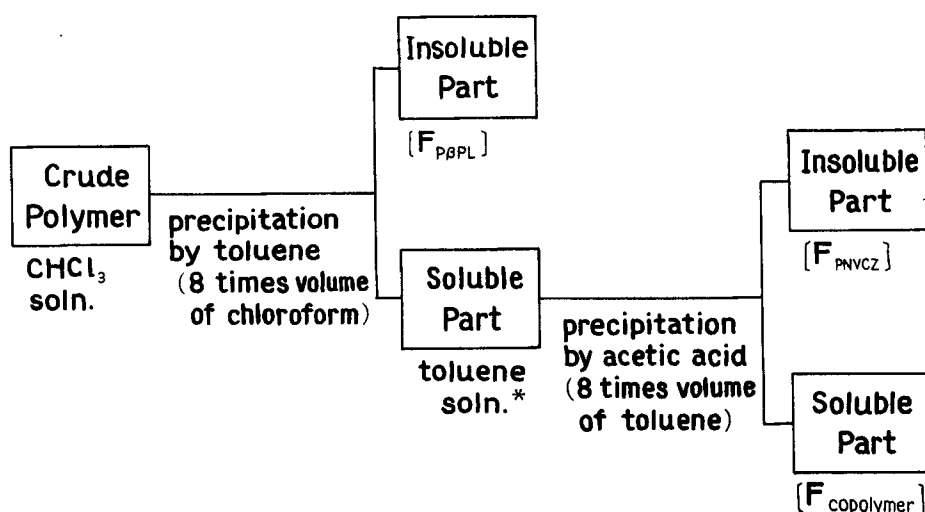


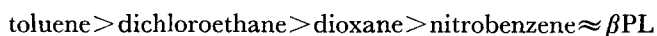
Fig. 1. Fractionation of the block copolymer

\* This soluble part is concentrated under reduced pressure and is dissolved again in toluene.

## Results and Discussion

### Simultaneous Polymerization in the Heterogeneous System

Mixture of  $\beta PL$  and NVCZ is polymerized simultaneously by both cationic and anionic catalysts. The heterogeneity of reaction system is changed by using various kinds of solvents having different solubilities for toluene sulfonic acid, sodium acetate, poly-N-vinylcarbazole (PNVCZ) and poly- $\beta$ -propiolactone ( $P\beta PL$ ), as shown in Table 1. The order of the heterogeneity seems to be approximately:



The time-conversion curves of simultaneous polymerization in heterogeneous

Table 1. Effect of Solvent at the Simultaneous Polymerization of NVCZ- $\beta$ PL by Cationic and Anionic Catalysts in Heterogeneous System.

Exp. no.	Solvent	Dielectric constant	Solubility			
			CH <sub>3</sub> COONa	CH <sub>3</sub> $\phi$ SO <sub>3</sub> H	P $\beta$ PL	PNVCZ
G90-2	Toluene	2.38	×	×	×	○
" 3	Dichloroethane	4.6	×	×	○	○
" 5	Dioxane	2.23	×	○	○	○
" 6	Nitrobenzene	34.8	×	○	○	△
" 4	$\beta$ -Propiolactone	42	△	○	○	×

Total conv. (%)	Fractionation [NVCZ cont.] (mole %)		
	F <sub>P<math>\beta</math>PL</sub>	F <sub>PNVCZ</sub>	F <sub>coPolym.</sub>
16.7	39.5[0]	43.7[87.7]	16.7[73.8]
15.6	2.1[0]	89.3[95.8]	9.4[47.2]
0.52	—	—	—
23.5	44.6[0]	50.1[98.0]	5.3[—]
57.3	79.2[0]	14.3[92.2]	6.56[20]

NVCZ 0.309 g,  $\beta$ PL 1.62 g, NVCZ content in monomer 6.6 mole %, solvent 6 cc. CH<sub>3</sub> $\phi$ SO<sub>3</sub>H  $6.6 \times 10^{-5}$  mole, CH<sub>3</sub>COONa  $6.6 \times 10^{-5}$  mole, 60°C, in N<sub>2</sub>, 19 hrs.

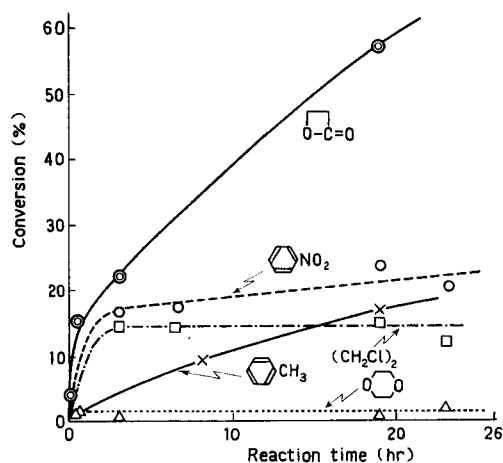


Fig. 2. Time-conversion curve at the simultaneous polymerization of  $\beta$ PL with NVCZ initiated by both cationic and anionic catalysts in heterogeneous system.

$\beta$ PL 4.5 cc, NVCZ 0.927 g, NVCZ in monomer 6.6 mole %, solvent 18 cc, CH<sub>3</sub> $\phi$ SO<sub>3</sub>H  $2 \times 10^{-4}$  mole, CH<sub>3</sub>COONa  $2 \times 10^{-4}$  mole, 60°C, in air.

system are represented in Fig. 2. in which three kinds of curve forms are observed as follows;

(1)  $\beta$ PL solution

The rate of polymerization is very large in the early stage, and then decreases but the conversion is still increasing. The growing ends seem to be terminated by the neutralization with cationic or anionic species, according to the higher

homogeneity of reaction system.  $\beta$ PL has been found to polymerize easily in bulk by sodium sulfonate produced by termination reaction as shown in our previous papers<sup>9)10)</sup>.

(2) Dichloroethane solution

The rate of polymerization in the early stage is not small but then the conversion reaches saturation. The termination reaction seems to occur easily according to high homogeneity of the system and also  $\beta$ PL has been found to polymerize with difficulty by sodium sulfonate in these solvents with low dielectric constants.

In the case of nitrobenzene solution the form of time-conversion curve is the middle one between the curves of (1) and (2).

(3) Toluene solution

The termination reaction between the catalysts with opposite charge seems to occur with difficulty in such a heterogeneous system as toluene, in which the polymerization shows normal behavior.

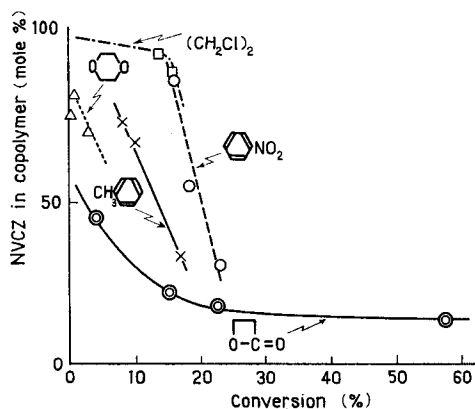
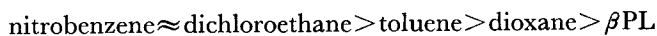


Fig. 3. Polymer composition at the simultaneous polymerization of  $\beta$ PL with NVCZ initiated by both cationic and anionic catalysts in heterogeneous system.

NVCZ contents in the polymers obtained by simultaneous polymerizations are shown in Fig. 3. The order of NVCZ contents in these polymers obtained in various kinds of solvents shows the following;



The polymers obtained in such solvents being suitable for cationic polymerization as nitrobenzene or dichloroethane contain the larger amounts of NVCZ units than those obtained in such solvents for anionic polymerization as dioxane. The effect of solvent on the simultaneous polymerization is summarized in Table 1. In the comparison within the experiments of No. G 90-2, 3 and 5, dielectric constants of these solvents are in same order, but the difference of heterogeneity of systems seems to be clear as the following order;

toluene > dichloroethane > dioxane

Thus the total conversions increase in this order. Concerning with the experiments of No. G 90-5, 6 and 4, the heterogenities of reaction systems are almost the same, although the dielectric constants of solvents change in the following order;

$\beta$ PL > nitrobenzene > dioxane

Thus the total conversions in these runs increase in this order. These results demonstrate that both the large heterogeneity and the high dielectric constant of medium seem to accelerate simultaneous polymerization. The results on the fractionation of obtained polymer are also shown in Table 1. Copolymer obtained probably by recombining between cationic and anionic growing ends is found to be soluble in both acetic acid and toluene.

### Simultaneous Polymerization in the Homogeneous System

Monomer mixture of NVCZ and  $\beta$ PL is first polymerized by sodium acetate in bulk (Fig. 4-a) and then the equivalent amount of *p*-toluene sulfonic acid is added into the polymerizing system (Fig. 4-b). The conversion increases immediately after the addition of cationic catalyst and then anionic and cationic polymerizations proceed simultaneously at least for about 3 hrs. Then the polymerization stops at about 40% of conversion. Anionic growing end of P $\beta$ PL, i.e., carboxyl anion seems to be relatively stable and also cationic end of growing P-NVCZ seems to be not so unstable. Therefore, simultaneous polymerization may occur even in the homogeneous systems.

The simultaneous polymerization in nitrobenzene solution is also carried out, as shown in Fig. 5. Time-conversion curves of polymerization by sodium acetate, *p*-toluene sulfonic acid and both of these catalysts are compared each other. In the anionic polymerization of  $\beta$ PL with NVCZ by sodium acetate (Fig. 5-a)  $\beta$ PL is mainly polymerized. Here the polymerization of NVCZ is thought to proceed in cationic mechanism by the acrylic acid produced by proton transfer reaction with  $\beta$ PL, or by the end carboxyl groups of P- $\beta$ PL. In the cationic polymerization of  $\beta$ PL with NVCZ by *p*-toluene sulfonic acid (Fig. 5-b), NVCZ polymerizes very rapidly but  $\beta$ PL does not polymerize under the condition investigated. The mixture of  $\beta$ PL and NVCZ is polymerized by sodium acetate in nitrobenzene and then after 48 hrs, *p*-toluene sulfonic acid-nitrobenzene solution is added into the above (anionic polymerization) system to polymerize simultaneously by both cationic and anionic catalysts (Fig. 5-c). Conversion of NVCZ increases rapidly by the addition of cationic catalyst, but  $\beta$ PL does not polymerize. In this case, the rate of cationic polymerization of NVCZ seems to be very much higher than that of  $\beta$ PL in anionic mechanism.

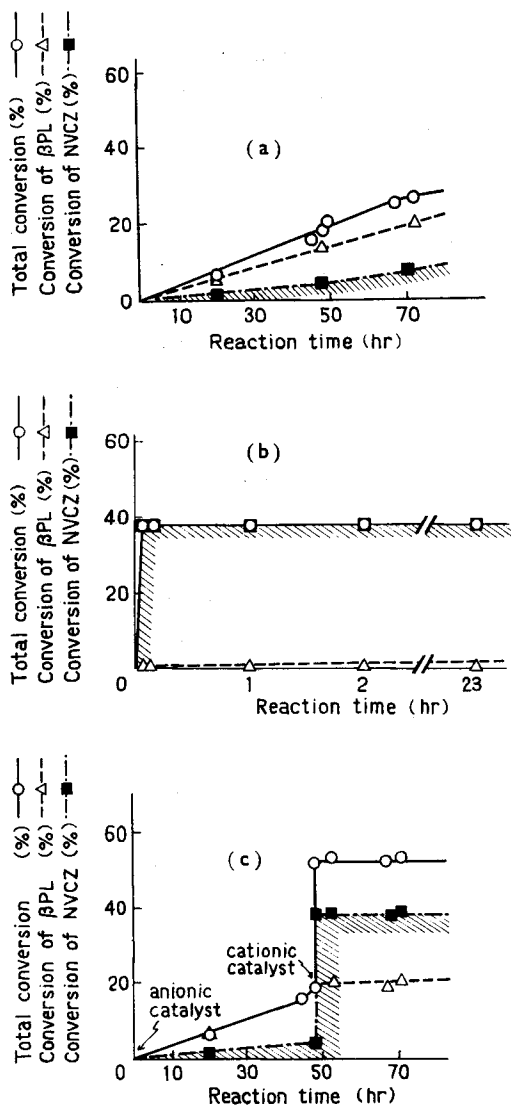


Fig. 5. Simultaneous polymerization of  $\beta$ PL with NVCZ by both cationic and anionic catalysts in homogeneous system in nitrobenzene.  $\beta$ PL 6.0 cc, NVCZ 4.66 g, NVCZ in monomer 20 mole %, nitrobenzene 27 cc,  $\text{CH}_3\phi\text{SO}_3\text{H}$   $3.3 \times 10^{-5}$  mole,  $\text{CH}_3\text{COONa}$   $3.3 \times 10^{-5}$  mole,  $60^\circ\text{C}$ , in air  
 (a) Anionic polymerization by  $\text{CH}_3\text{COONa}$   
 (b) Cationic polymerization by  $\text{CH}_3\phi\text{SO}_3\text{H}$   
 (c) Cationic catalyst was added into anionic polymerization system.

### Cationic Polymerization in the presence of Anionic Catalyst

Anionic growing end of P- $\beta$ PL is found to be sodium carboxyl group.<sup>4)</sup> It is recognized that NVCZ polymerizes even in the presence of sodium acrylate. Then some cationic (polymerizable) monomers such as NVCZ, iBVE,  $\alpha$ MeSt or TOX are examined for polymerizing in the presence of anionic catalyst (Tables 2 and 3). As shown in Table 2, NVCZ polymerizes even in the presence of butyl lithium (BuLi) which is a typical, strong anionic catalyst. This fact demonstrates that the cationic growing end of P-NVCZ seems to be relatively stable. When NVCZ,

Table 2. Cationic Polymerization of NVCZ in the Presence of Anionic Catalyst.

Exp. no.	Anionic catalyst ( $\times 10^{-6}$ mole)	Cationic catalyst ( $\times 10^{-6}$ mole)	Solvent
G108- 2	$C_{17}H_{35}COONa$ 3.5	$CH_3\phi SO_3H$ 3.3	Nitrobenzene
G101- 4	" 3.5	" 3.3	Dioxane
G101- 6	" 10.0	" 3.3	"
G107-19	BuLi 3.5	$BF_3OEt_2$ 3.3	Toluene

Temp. ( $^{\circ}C$ )	Time (min.)	Conversion (%)	$[\eta]$ in benzene at $25^{\circ}C$ ,
60	10	96.0 (100.0)*	0.093 (0.096)*
"	30	25.3 ( 28.0)*	0.030 (0.031)*
"	30	0 ( 28.0)*	— (0.031)*
10	30	99.6 (100.0)*	0.43 (0.48)*

1 cc of cationic catalyst solution is added to 2 cc of NVCZ-solution containing anionic catalyst; NVCZ, 0.3 g; solvent, 3 cc

\*...the absence of anionic catalyst.

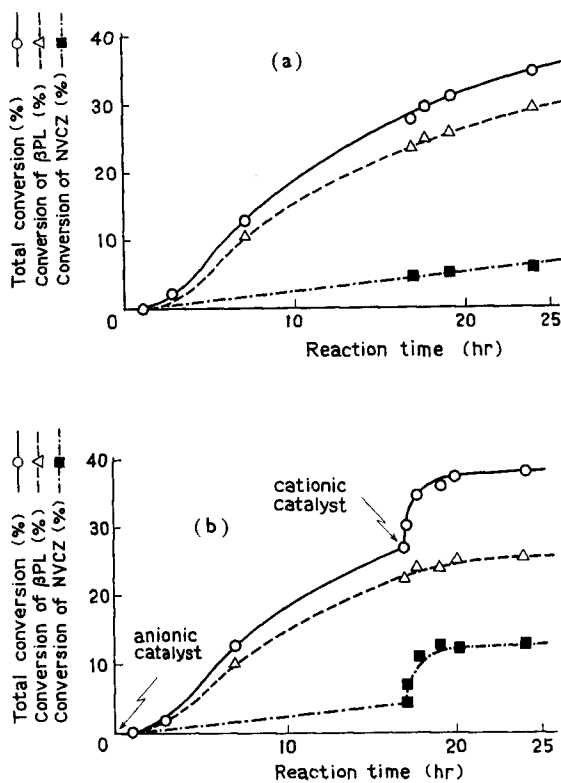


Fig. 4. Simultaneous polymerization of  $\beta$ PL with NVCZ by both cationic and anionic catalysts in homogeneous system in bulk.

$\beta$ PL 10.9 g, NVCZ 2.05 g, NVCZ in monomer 6.5 mole %,  $CH_3COONa$   $3.0 \times 10^{-4}$  mole,  $CH_3\phi SO_3H$   $3.0 \times 10^{-4}$  mole,  $60^{\circ}C$ , in air

(a) anionic polymerization by  $CH_3COONa$ .

(b) cationic catalyst is added into anionic polymerization system.



Table 3. Cationic Polymerization of Various Cationic-active Monomers in the Presence of Anionic Catalyst

Exp. no.	Monomer	Anionic catalyst	Cationic catalyst	Solvent
	(cc)	(mole)	(mole)	(cc)
G101- 4 (1)	NVCZ 0.3 g	$C_{17}H_{35}COONa$ $3.5 \times 10^{-6}$	$CH_3\phi SO_3H$ $3.3 \times 10^{-6}$	Dioxane 3
G102- 2 (5)	iBVE 0.5	"	"	"
G102- 4 (6)	$\alpha$ MeSt 0.5	"	"	"
G107-18	NVCZ 0.3 g	BuLi $3.5 \times 10^{-6}$	$BF_3OEt_2$ $3.3 \times 10^{-6}$	Toluene 3
G108- 2	iBVE 0.5	$C_{17}H_{35}COONa$ $3.5 \times 10^{-6}$	"	Nitrobenzene 2 + Toluene 3
G108- 3	$\alpha$ MeSt 0.5	"	"	"
G108- 1	TOX 0.5	"	"	"
G111- 8(10)	$\alpha$ MeSt 1.0	St-DVB-ANa copolymer. 50 mg	Sulfonated St-DVB copolymer. 50 mg	Toluene 3 cc
G111- 9(10)	"	St-DVB-4VP copolymer. 50 mg	"	"

Temp. (°C)	Time (min.)	Conversion (%)	
		in the presence of anionic catalyst	in the absence of anionic catalyst
60	30	25.3	28.0
20	240	0	4.0
20	240	0	1.1
60	10	98.5	100
0	15	59.9	62.0
-4	15	0	6.2
60	960	0	64.6
0	1260	6.0	8.4
0	"	6.6	8.4

iBVE,  $\alpha$ MeSt and TOX are polymerized by *p*-toluene sulfonic acid in the presence of sodium acetate, only the NVCZ unit polymerizes. On the other hand, by boron trifluoride etherate ( $BF_3OEt_2$ ) (a strong cationic catalyst) in the presence of sodium acetate (a weak anionic catalyst) in nitrobenzene, iBVE, less active monomer for

cationic polymerization than NVCZ, polymerizes. In the case of polymerization initiated by sulfonated [styrene (St) - divinyl benzene (DVB)] copolymer, (an insoluble cationic catalyst) in the coexistence of [St-DVB-4 vinyl pyridine (4VP)] copolymer or [St-sodium acrylate (ANa)] copolymer, (an insoluble anionic catalyst),  $\alpha$ MeSt polymerizes. Thus even relatively less reactive monomer for cationic polymerization can also polymerize in the presence of anionic catalyst in heterogeneous system.

### Conclusion

In the simultaneous polymerization of  $\beta$ PL and NVCZ induced by the solid catalysts in the mixture of *p*-toluene sulfonic acid and sodium acetate, the heterogeneous system and the high dielectric constant of solvent seems to be favourable for the simultaneous polymerization induced by both cationic and anionic mechanisms. The simultaneous polymerization of  $\beta$ PL and NVCZ proceeds even in the homogeneous system because of the system having relatively stable growing ends. In order to polymerize simultaneously, it seems to be necessary that termination reactions between cationic catalyst or anionic catalyst and growing ends do not take place and the rates of cationic and anionic propagation may be approximately in the same order.

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