The Copolymerization of the Vinyl Monomer with a Cyclic Compound. II. The Cationic Copolymerization of Some Vinyl Monomers with β-Propiolactone*

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In a preceding paper,⁽¹⁾ the cationic copolymerization of some vinyl monomers with 3, 3-bis(chloromethyl)oxetane catalyzed by Lewis acids was investigated. It was found that the copolymers were not obtained in all systems, but that mixtures of the corresponding homopolymers were produced in some cases. The present paper is concerned with the cationic copolymerization of vinyl monomers with β-propiolactone (β-PL) catalyzed by Lewis acids.

It is interesting to prepare the copolymer of the vinyl monomer with β-PL, which gives the ester linkage in the main chain of the resulting copolymer. With such a purpose in mind, Okamura et al.,⁽²⁾ for instance, attempted the radiation-induced copolymerization of styrene (St), acrylonitrile and methyl methacrylate with β-PL. Shimosaka, Tsuruta and Furukawa⁽³⁾ prepared the copolymer of acrylonitrile with β-PL through the copolymerization catalyzed by organometallic compounds. Yamashita et al.⁽⁴⁾ reported the copolymerization of St with β, β-dimethyl-β-propiolactone by stannic chloride.

In the present paper, St, α-methylstyrene (α-MeSt) and isobutyl vinyl ether (IBVE) will be used as vinyl monomers. Boron trifluoride-diethyl etherate ($BF_3 \cdot Et_2O$), stannic chloride ($SnCl_4$) and triethylaluminum-water ($AlEt_3$-H_2O) will be used as cationic catalysts. From the copolymerization results, the reactivity of β-PL with vinyl monomers will be evaluated and discussed.

Experimental

Materials.—Commercial β-PL, St, α-MeSt and IBVE were distilled over calcium hydride under reduced pressures.

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* Vinyl Polymerization. CV.

1) S. Aoki, Y. Harita, T. Otsu and M. Imoto, This Bulletin, **38**, 1922 (1965).

2) S. Okamura, K. Hayashi, Y. Kitanishi and M. Nishii, *Isotopes and Radiation* (*Doitai to Hoshasen*), 3, 510 (1960).

3) Y. Shimosaka, T. Tsuruta and J. Furukawa, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 1498 (1963).

4) Y. Yamashita, T. Tsuda, Y. Ishikawa and T. Shimizu, ibid., **66**, 1493 (1963).

$BF_3\cdot Et_2O$, $SnCl_4$ and methylene chloride were purified and the $AlEt_3$-H_2O catalyst was prepared in the methods described in the preceding paper.[1] The other materials were purified by the ordinary methods.

Copolymerization Procedure.—The copolymerization procedure was the same as that described in the preceding paper.[1]

The Fractionation of the Polymer.—The polymer obtained in the copolymerization of β-PL and St was fractionated to determine whether this polymer was the copolymer or a mixture of the homopolymers. Since polySt was isoluble in acetic acid, while polyβ-PL was soluble, the chloroform solution of the resulting polymer was poured into a large amount of acetic acid in order to separate it into acetic acid-soluble and acetic acid-insoluble fractions. Both fractions were then further fractionated by the chloroform-methanol system.

The Analysis of the Polymer.—The compositions of the polymers obtained in various monomer compositions were determined by means of their infrared spectra and by means of elementary analyses on carbon.

The molecular weight of the polymer was determined with a Mechrolab vapor pressure osmometer, model 301-A.

The inherent viscosity of the polymer was measured in a one per cent solution of it in choroform at 30°C.

Results

The β-PL - St - $BF_3\cdot Et_2O$ or - $SnCl_4$ System.—The results of the copolymerization of β-PL with St catalyzed by $BF_3\cdot Et_2O$ or $SnCl_4$ are summarized in Tables I and II. The copolymerization proceeded without difficulty with both catalysts, and a colorless, powdered polymer was obtained. The infrared spectra of the resulting polymer showed the characteristic absorption bands at 1725 and 1603 cm^{-1} based on the ester linkage (β-PL unit) and

TABLE I. COPOLYMERIZATION OF St AND β-PL BY $BF_3\cdot Et_2O$ IN METHYLENE CHLORIDE AT 0°C ([Monomer]=3, [$BF_3\cdot Et_2O$]=0.07 mol./l.)

Exp. No.	Monomer compn.*		Time min.	Conversion %	R_p %/min.	Polymer resulted					
						I.R.S.**		Analysis***		Compn.*	
	St	β-PL				St	β-PL	C%	H%	St	β-PL
11	1.00	0.00	0.5	89	187	(+)	(−)	(92.26)	(7.74)	1.00	0.00
12	0.60	0.40	8	2.9	0.36			91.34	7.99	0.97	0.03
13	0.50	0.50	5	2.2	0.45	+	+	90.88	7.68	0.95	0.05
14	0.40	0.60	65	2.7	0.04	+	+	90.20	7.74	0.93	0.07
15	0.30	0.70	30	1.6	0.05	+	+	89.68	7.66	0.91	0.09
16	0.20	0.80	60	0.7	0.01	+	+	83.49	7.30	0.73	0.27
17	0.00	1.00	900	8.8	0.01	(−)	(+)	(49.99)	(5.61)	0.00	1.00

* In mole fraction
** Infrared spectrum
*** Figures in parentheses are the calculated value.

TABLE II. COPOLYMERIZATION OF St AND β-PL BY $SnCl_4$ IN METHYLENE CHLORIDE AT 0°C ([Monomer]=3, [$SnCl_4$]=0.07 mol./l.)

Exp. No.	Monomer compn.*		Time min.	Conversion %	R_p %/min.	Polymer resulted					
						I.R.S.		Analysis		Compn.*	
	St	β-PL				St	β-PL	C%	H%	St	β-PL
21	1.00	0.00	2	35	18	(+)	(−)	—	—	1.00	0.00
22	0.60	0.40	2.5	15.8	6.3	+	+	90.53	7.96	0.94	0.06
23	0.60	0.40	2	21.8	10.9	+	+	90.45	7.79	0.94	0.06
24	0.50	0.50	4	16.8	4.2	+	+	90.30	7.80	0.93	0.07
25	0.50	0.50	3	19.2	6.4	+	+	90.62	7.77	0.94	0.06
26	0.40	0.60	6.5	13.7	2.1	+	+	89.85	7.68	0.92	0.08
27	0.40	0.60	4	13.8	3.4	+	+	90.09	7.89	0.93	0.07
28	0.30	0.70	8	8.6	1.1	+	+	89.55	7.69	0.91	0.09
29	0.30	0.70	7	8.0	1.1	+	+	89.06	7.67	0.89	0.11
30	0.20	0.80	12	6.2	0.5	+	+	82.21	7.23	0.69	0.31
31	0.20	0.80	9.5	4.2	0.4	+	+	85.95	7.50	0.80	0.20
32	0.00	1.00	80	29.3	0.4	(−)	(+)	—	—	0.00	1.00

* In mole fraction

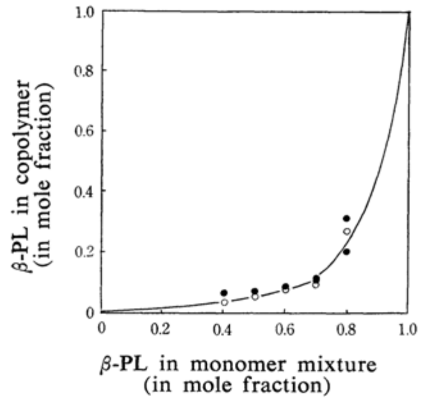


Fig. 1. Monomer-polymer composition curve for the copolymerization of St and β-PL. (○) $BF_3 \cdot Et_2O$ catalyst, (●) $SnCl_4$ catalyst

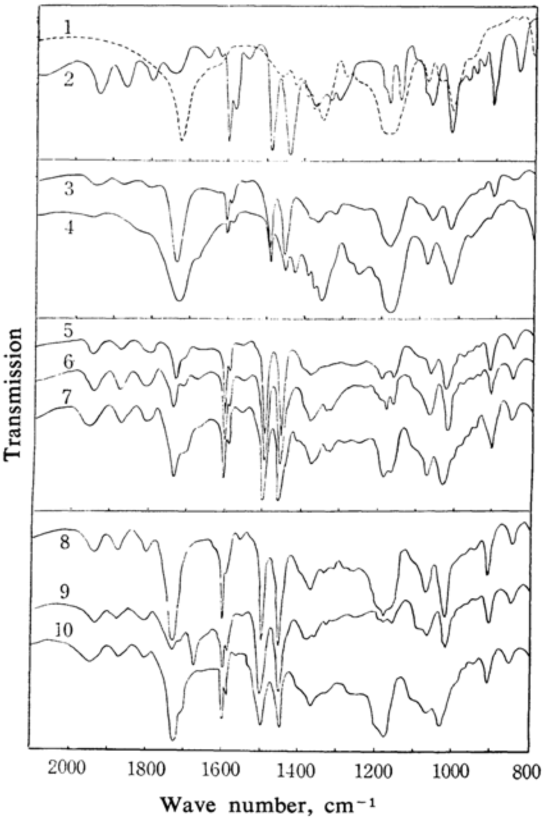


Fig. 2. Infrared spectra of the β-PL - St copolymer (in KBr disk).
1. Poly-β-PL, 2. PolySt, 3. No. 16 unfractionated, 4. No. 16 AcOH-soluble, 5. No. 24 unfractionated, 6. No. 24 AcOH-isoluble, 7. No. 24 AcOH-soluble, 8. No. 28 unfractionated, 9. No. 28 AcOH-insoluble, 10. No. 28 AcOH-soluble

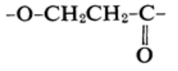
the benzene nucleus (St unit) respectively (see Fig. 2). The monomer-polymer composition curve for this copolymerization is shown in Fig. 1.

No difference between $BF_3 \cdot Et_2O$ and $SnCl_4$ catalysts was observed in the monomer-polymer composition relation. The apparent monomer reactivity ratios were estimated, by the curve-fitting method, to be $r_{(\beta\text{-PL})}=0.2$ and $r_{(St)}=20$ respectively.

In order to determine whether the polymer obtained here was the copolymer or a mixture of the corresponding homopolymers, the resulting polymer was fractionated into several fractions. The results are given in Table III, while the infrared spectra of soluble and insoluble fractions in acetic acid are shown in Fig. 2.

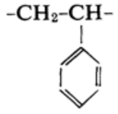
It was proved, by infrared spectra and elementary analysis, that the insoluble fraction of the resulting copolymer in acetic acid, which is known to be a solvent for only polyβ-PL, contained the β-PL unit; while its soluble fraction contained the St unit. The molecular weight of the fractionated copolymer was not very low (see Table III). These results indicated that the copolymer of β-PL with St was produced in their copolymerizations with such Lewis acids as $BF_3 \cdot Et_2O$ and $SnCl_4$.

Some of the infrared spectra of the unfractionated and fractionated copolymers showed absorption bands at 1680 and 1710 cm^{-1} in addition to the characteristic bands mentioned above (see Fig. 2). It is assumed that the structure of the β-PL - St copolymer contains the following four types of repeating units:

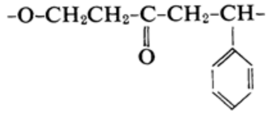


$-O-CH_2CH_2-\underset{\overset{\|}{O}}{C}-$

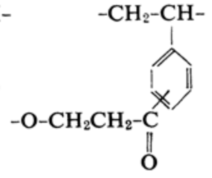
(I)



(II)



(III)



(IV)

The structures I and II are the repeating units of polyβ-PL and polySt, and show the characteristic absorption bands in the infrared spectra at 1725 and 1603 cm^{-1} respectively. The structure III must be formed through the copolymerization in which the opening of the β-PL ring, followed by an attack on the vinyl double bond of St, takes place to form carbonyl cations as the propagating species. Since the infrared absorption band at 1710 cm^{-1} agreed with that of a carbonyl group of aliphatic ketone, it was obvious that this copolymer contained the structure III. If the carbonyl cation formed from β-PL attacks the benzene nucleus of monomeric or polymeric St through the chain-transfer reaction, the structure IV may be formed. The absorption band at 1680 cm^{-1} may be assigned to a carbonyl group of aromatic ketone. It was therefore concluded that this copolymer contained the structure IV.

In order to obtain further evidence for the existence of the structure IV in the copolymer, the polymerization of β-PL in the presence of ethylbenzene in place of St was performed. The existence of the ketonic carbonyl group in the resulting polymer was also confirmed by the reaction with 2, 4-dinitrophenylhydrazine.

The β-PL - St - $AlEt_3$-H_2O System.—The results of the copolymerization of β-PL with St catalyzed by $AlEt_3$-H_2O are summarized in Table IV. In contrast with the case of the $BF_3 \cdot Et_2O$ or the $SnCl_4$ catalyst, no copolymer was obtained in this catalyst system.

The β-PL - α-MeSt - $BF_3 \cdot Et_2O$ or - $SnCl_4$ System.—The results of the copolymerization of β-PL with α-MeSt by the $BF_3 \cdot Et_2O$ or the $SnCl_4$ catalyst are summarized in Tables V and VI. The absence of the β-PL unit in the resulting polymers was confirmed by their infrared spectra.

The β-PL - α-MeSt - $AlEt_3$-H_2O System.—The results of the copolymerization of β-PL and α-MeSt by the $AlEt_3$-H_2O catalyst are shown in Table VII. The resulting polymers were found to be homopolymers of β-PL, much as in the case of β-PL - St - $AlEt_3$-H_2O.

The β-PL - IBVE - $SnCl_4$ System.—The results of the copolymerization of β-PL and IBVE by $SnCl_4$ are tabulated in Table VIII. The polymerization was very rapid, and the resulting

TABLE III. FRACTIONATION OF THE β-PL - St COPOLYMER

Fraction	Wt., g.	Wt., %	Analysis		Composition	
			C%	H%	St	β-PL
			Exp. No. 24			
Sample	0.294_9	—	90.30	7.79	0.93	0.07
1	0.194_1*	65.8	90.59	8.05	0.94	0.06
2 (Insoluble in acetic acid)	0.008_6	2.9	86.64	8.14	0.82	0.18
3 (Soluble in acetic acid)	0.067_2**	22.8	85.91	7.76	0.80	0.20
			Exp. No. 28			
Sample	0.170_6	—	89.55	7.69	0.91	0.09
1 (Insoluble in acetic acid)	0.035_5	20.8	90.29	7.78	0.93	0.07
2	0.063_2	37.1	85.32	7.57	0.78	0.22
3	0.017_5	5.9	—	—	—	—
4 (Soluble in acetic acid)	0.033_3	19.5	82.67	7.41	0.70	0.30

* Molecular weight 3250

** Molecular weight 2120

TABLE IV. COPOLYMERIZATION OF St AND β-PL BY $AlEt_3$-H_2O IN METHYLENE CHLORIDE AT 0°C
([Monomer] = 3, [$AlEt_3$-H_2O] = 0.07 mol./l.)

Exp. No.	Monomer compn.*		Time min.	Conversion, %	$R_p \times 10^3$ %/min.	I.R.S. of polymer	
	St	β-PL				St	β-PL
41	1.00	0.00	180	0.2	0.9	(+)	(−)
42	0.80	0.20	420	3.3	7.8	−	+
43	0.60	0.40	420	1.2	2.9	−	+
44	0.50	0.50	420	1.2	2.9	−	+
45	0.40	0.60	420	2.0	4.8	−	+
46	0.30	0.70	1365	3.2	2.4	−	+
47	0.20	0.80	630	0.7	1.1	−	+
48	0.00	1.00	100	0.2	2.0	(−)	(+)

* In mole fraction

TABLE V. COPOLYMERIZATION OF α-MeSt AND β-PL BY $BF_3 \cdot Et_2O$ IN METHYLENE CHLORIDE AT 0°C
([Monomer]=3, $[BF_3 \cdot Et_2O]=0.07$ mol./l.)

Exp. No.	Monomer compn.*		Time min.	Conversion, %	R_p %/min.	I.R.S. of polymer	
	α-MeSt	β-PL				α-MeSt	β-PL
51	1.00	0.00	0.75	53.4	71	(+)	(−)
52	0.80	0.20	2	22.5	11.3	+	−
53	0.70	0.30	0.5	6.9	13.9	+	−
54	0.60	0.40	0.5	7.2	15.0	+	−
55	0.50	0.50	11	19.9	1.8	+	−
56	0.40	0.60	1	5.0	5.0	+	−
57	0.30	0.70	2	2.1	1.1	+	−
58	0.20	0.80	2	0.2	0.1	+	−
17	0.00	1.00	900	8.8	0.01	(−)	(+)

* In mole fraction

TABLE VI. COPOLYMERIZATION OF α-MeSt AND β-PL BY $SnCl_4$ IN METHYLENE CHLORIDE AT 0°C
([Monomer]=3, $[SnCl_4]=0.07$ mol./l.)

Exp. No.	Monomer compn.*		Time sec.	Conversion, %	R_p %/min.	I.R.S. of polymer	
	α-MeSt	β-PL				α-MeSt	β-PL
61	1.00	0.00	30	73	147	(+)	(−)
62	0.80	0.20	135	54	24	+	−
63	0.70	0.30	75	29.8	23.8	+	−
64	0.60	0.40	60	30.0	30.0	+	−
65	0.50	0.50	90	19.8	12.7	+	−
66	0.40	0.60	60	8.7	8.7	+	−
67	0.30	0.70	120	5.9	2.9	+	−
68	0.20	0.80	215	1.6	0.4	+	−
32	0.00	1.00	4800	29.3	0.4	(−)	(+)

* In mole fraction

TABLE VII. COPOLYMERIZATION OF α-MeSt AND β-PL BY $AlEt_3$-H_2O IN METHYLENE CHLORIDE AT 0°C
([Monomer]=3, $[AlEt_3\text{-}H_2O]=0.07$ mol./l.)

Exp. No.	Monomer compn.*		Time min.	Conversion, %	$R_p \times 10^3$ %/min.	I.R.S. of polymer	
	α-MeSt	β-PL				α-MeSt	β-PL
71	1.00	0.00	2550	0.03	0.01	(+)	(−)
72	0.70	0.30	2550	1.1	0.4	−	+
73	0.50	0.50	1400	0.9	0.7	−	+
74	0.40	0.60	1450	0.9	0.7	−	+
75	0.20	0.80	1450	1.3	0.9	−	+
48	0.00	1.00	100	0.2	2.0	(−)	(+)

* In mole fraction

TABLE VIII. COPOLYMERIZATION OF IBVE AND β-PL BY $SnCl_4$ IN METHYLENE CHLORIDE AT 0°C
([Monomer]=3, $[SnCl_4]=0.07$ mol./l.)

Exp. No.	Monomer compn.*		Time sec.	Conversion, %	R_p %/min.	I.R.S. of polymer	
	IBVE	β-PL				IBVE	β-PL
81	1.00	0.00	5	69	830	(+)	(−)
82	0.60	0.40	5	29.9	357	+	−
83	0.50	0.50	5	27.2	326	+	−
84	0.40	0.60	5	19.8	237	+	−
85	0.20	0.80	10	5.0	30	+	−
32	0.00	1.00	4800	29.3	0.4	(−)	(+)

* In mole fraction

polymer was confirmed by infrared spectra to be polyIBVE.

Discussion

The results of the copolymerization of vinyl monomers with β-PL are summarized in Table IX. As this table shows, the β-PL - St - $BF_3\cdot Et_2O$ or - $SnCl_4$ system gave copolymer. This copolymer contained infrared absorption bands at 1680 and 1710 cm^{-1} which could be assigned to the carbonyl groups of aromatic and aliphatic ketones respectively. These results indicate that the ring-opening of β-PL takes place at the acyl-oxygen bond, as has been reported by Cherdron et al.[5] The presence of aromatic and aliphatic ketones also indicates that the copolymers obtained here include a graft copolymer of polySt containing a pendant polyester chain derived from β-PL.

In our previous paper,[1] it was suggested that the copolymer was not obtained in the copolymerization of monomers which propagate via different propagating species, carbonium and oxonium ions. Accordingly, the fact that the copolymer is formed in the present case may lead to the conclusion that the propagating species of β-PL in this cationic polymerization is that of carbonium ions, although an oxonium-ion mechanism was proposed by Yamashita et al.[6]

TABLE IX. COPOLYMERIZATION BEHAVIOR OF β-PL

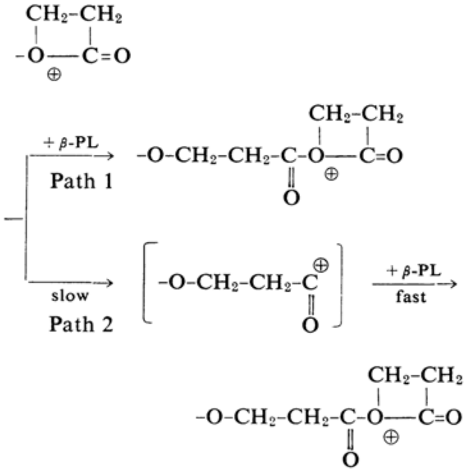
Catalyst	Comonomer		
	St	α-MeSt	IBVE
$BF_3\cdot Et_2O$	Copolymer	Polyα-MeSt	—
$SnCl_4$	Copolymer	Polyα-MeSt	PolyIBVE
$AlEt_3$-H_2O	Polyβ-PL	Polyβ-PL	—

TABLE X. HOMOPOLYMERIZATION OF β-PL BY $SnCl_4$ IN METHYLENE CHLORIDE AT 0°C
([$SnCl_4$]=0.07 mol./l.)

[β-PL] mol./l.	Time min.	Conversion, %	$R_p\times10^3$ mol./l. min.	η_{sp}/C* dl./g.
0.5	270	36.5	0.7	0.07
1.0	150	28.3	1.9	0.07
2.0	250	35.2	2.8	0.09
2.0	345	46.6	2.7	0.09
3.0	80	29.3	11.0	0.09

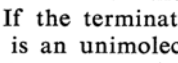
* In 1% chloroform solution at 30°C.

In order to clarify this ambiguity, the homopolymerization of β-PL was undertaken. The results are tabulated in Table X. The rate of polymerization increased with an increase in the concentration of the monomer, but the molecular weight of the resulting polymer, as deduced from its inherent viscosity, was little affected. The propagation scheme in β-PL polymerization may, then, be expressed by the following two paths:



In path 1, an oxonium ion of the propagating β-PL directly attacks the β-PL monomer. On the other hand, in path 2, the propagation includes a carbonium-ion intermediate. From the difference in the stabilities of the oxonium and carbonium ions, it may reasonably be assumed that, in path 2, the rate-determining step is the formation of the carbonium-ion intermediate. If the termination of the β-PL polymerization is an unimolecular reaction of the growing cation, the molecular weight of the resulting polymer is proportional to the monomer concentration in path 1, while it is independent of it in path 2.

The results in Table X support the mechanism of path 2. In practice, however, the carbonyl cation derived from β-PL may be considered to exist as an intramolecular-solvated state, an intermediate between oxonium and carbonium ions. Therefore, the β-PL-growing cation contains an intermediate structure of both oxonium and carbonium ions (V):



(V)

In a polar solvent the character of the carbonium ion may be emphasized, but the reverse holds in a nonpolar solvent. Thus, it may be concluded that β-PL copolymerizes with St via β-PL carbonium ions and with 3, 3-bis(chloromethyl)oxetane[7] via oxonium ions.

The reaction scheme of the copolymerization of β-PL and St can be given as follows:

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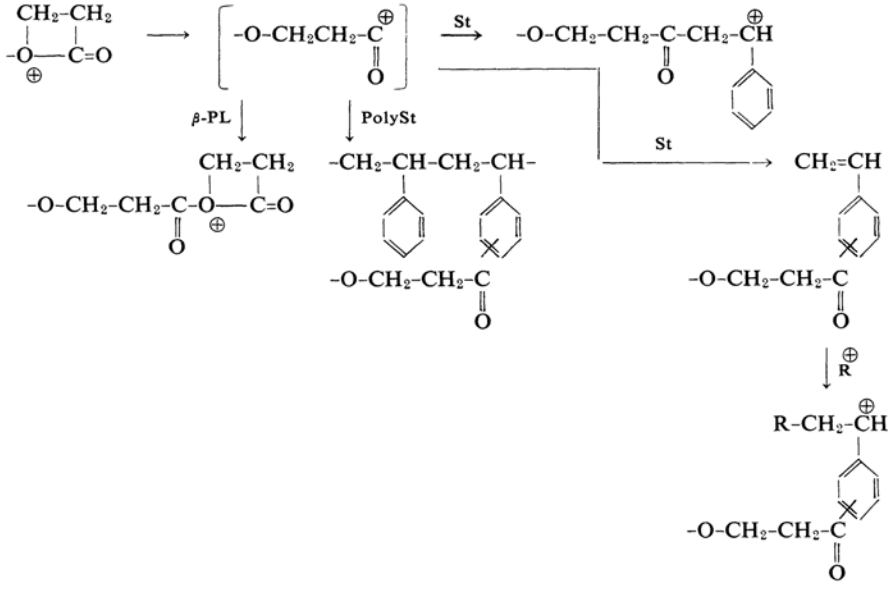
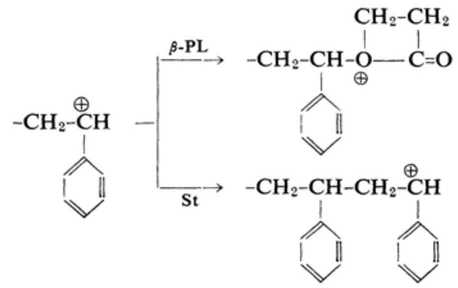
[5] H. Cherdron, H. Ohse and F. Korte, *Makromol. Chem.*, **56**, 179 (1962).

[6] Y. Yamashita, Y. Ishikawa, T. Tsuda and S. Miura, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 104 (1963).

[7] K. Tada, T. Saegusa and J. Furukawa, *Makromol. Chem.*, **71**, 71 (1964).





It should be noted that the copolymerization results on α-MeSt and IBVE by $BF_3 \cdot Et_2O$ or $SnCl_4$, as shown in Table IX, may be understood to be caused by the higher reactivity of these vinyl monomers than that of St. The difference between the results obtained using $BF_3 \cdot Et_2O$ and $SnCl_4$, and $AlEt_3$-H_2O as catalysts may result from the difference in the effect of gegen ions.

Summary

The copolymerization of several vinyl monomers, such as styrene (St), α-methylstyrene and isobutyl vinyl ether, with β-propiolactone (β-PL) as catalyzed by Lewis acids has been investigated in methylene chloride at 0°C. In the copolymerization of β-PL and St using boron trifluoride-diethyl etherate or stannic chloride as a catalyst, the copolymer was obtained. The apparent monomer reactivity ratios were estimated to be as follows:

$$r_{(\beta\text{-PL})}=0.2\,;\quad r_{(\mathrm{St})}=20$$

In the other copolymerization systems, the copolymer was not obtained. The mechanism of these copolymerizations has been discussed.

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