

Ionic Graft Copolymerization. IV. Polymerization of β -Propiolactone by Acetic Acid, *p*-Toluenesulfonic Acid, and Their Sodium Salts

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Synopsis

Acetic acid, toluenesulfonic acid, and their salts are used as four representative ionic catalysts for polymerization of β -propiolactone (β PL). They are classified as follows: sodium acetate is an anionic catalyst, acetic acid is a neutral one having more covalent character, sodium toluene sulfonate is a neutral one having more ionic character, toluenesulfonic acid is a cationic one. The neutral catalyst having more covalent nature is hardly dissociated, and therefore the rate of polymerization is quite small; however, dissociated ions consist of a higher nucleophilic anion and a higher electrophilic cation. On the contrary, the neutral catalyst having an ionic bond dissociates more easily, but the formed ions consist of the less reactive anion and cation. Therefore, it is of interest whether β -propiolactone is polymerized by a cationic mechanism or an anionic mechanism by these catalysts. The mechanisms of polymerizations of β PL by these neutral catalysts were studied on the basis of the different behaviors of polymerizations by the four catalysts described above. In the cationic polymerization by toluenesulfonic acid, the rate of polymerization was high, but the conversion reaches a low, limited value. In the anionic polymerization by sodium acetate, the rate of polymerization was high and the degree of polymerization of polymer was the highest. Acetic acid has the lowest catalyst activity and the degree of polymerization is also very small. It was found that the polymerization by sodium *p*-toluenesulfonate was accelerated in the presence of acrylic acid produced from β PL by hydrogen-transfer reaction.

INTRODUCTION

In our previous papers,^{1,2} the polymerization of β -propiolactone (β PL) by alkali metal carboxylate and the graft copolymerization of β PL onto polyacrylonitrile containing the COONa group were investigated.

In the present paper, the mechanisms of polymerization of β PL by neutral catalysts intermediate in nature between anionic catalyst and cationic catalyst were investigated in comparison with those obtained with sodium acetate, acetic acid, sodium sulfonate, and sulfonic acid.

The catalysts used here are four representative ionic catalysts; sodium acetate is an anionic catalyst, acetic acid is a neutral catalyst having more covalent character which lies between an anionic catalyst and a cationic one, sodium toluene sulfonate is a neutral catalyst having more ionic character, and toluenesulfonic acid is a cationic catalyst.

The neutral catalyst having a more covalent nature is hardly dissociated and therefore the rate of polymerization is quite small. However dissociated pair ions consist of an anion of higher nucleophilicity and a cation of higher electrophilicity.

On the other hand, the neutral catalyst having ionic nature dissociates more easily, but dissociated pair ions consist of the less reactive anion and cation. Therefore, it is of interest whether polymerization of β PL proceeds by a cationic mechanism or an anionic mechanism with these catalysts.

The mechanisms of polymerizations of β PL by neutral catalysts were studied, the polymerization behaviors with the four catalysts mentioned above being compared.

The present study was carried out with the object of investigation of homopolymerization of β PL in comparison with the graft copolymerization.³

In the cationic polymerization by *p*-toluenesulfonic acid, the rate of polymerization was high, but the conversion reaches a limiting low value.

In the anionic polymerization by sodium acetate, the rate of polymerization was high, and the degree of polymerization of polymer was higher than that of polymers obtained with acetic acid, sodium toluene sulfonate, and toluene sulfonic acid.

Acetic acid has the lowest polymerization activity and the degree of polymerization is also very low.

It was found that the polymerization by sodium toluenesulfonate was accelerated in the presence of acrylic acid produced from β PL by the hydrogen-transfer reaction.

EXPERIMENTAL

Reagents

The purification of β PL was the same as previously described.¹

Toluene, acetic acid, and acrylic acid were purified by the usual procedures.

Toluenesulfonic acid was used as received (Nakarai Chemicals, Ltd. G. R. Grade).

Sodium acetate and sodium toluenesulfonate were prepared by careful neutralization of the corresponding acid and base respectively, and were recrystallized three times from aqueous solution.

Polymerization Procedure

Polymerization was carried out in a glass tube of 11 mm diameter under reduced pressure at 60°C as shown in the previous paper.¹

In the case of the polymerization by toluenesulfonic acid, β PL was polymerized in nitrogen stream and the reaction was terminated by addition of methanol containing a small amount of ammonia (ca. 0.05%). The conversions were determined by weighing the insoluble polymer in CH₃OH

in comparison to thermal, CH_3COOH -catalyzed, and dilatometric polymerization.

Analysis of βPL

βPL in sample solution was reacted with excess thiosulfate, and then unreacted thiosulfate was titrated by iodine solution.⁴

Analysis of Acrylic Acid in βPL

Acrylic acid in the reaction mixture was brominated with a potassium bromate-potassium bromide mixture in aqueous solution, and unreacted bromine was titrated by standard thiosulfate solution.⁴

Measurement of Intrinsic Viscosity and Determination of Endgroups

Measurement of intrinsic viscosity and determination of endgroups were the same as described in our previous paper.¹ The molecular weight was determined by a viscometric method.¹

RESULTS

Polymerization in Bulk

Polymerization of βPL by sodium acetate in bulk was reported previously.¹

Bulk Polymerization of βPL by Acetic Acid. The results of the bulk polymerization by acetic acid are presented in Table I.

The rate of polymerization and the degree of polymerization are very small, and therefore this polymerization was carried out under severe experimental conditions.

The thermal polymerization of βPL in bulk was carried out for purposes of comparison with that by acetic acid (Table II).

It was observed that the rate of bulk polymerization by acetic acid was of a similar order of magnitude as that of thermal polymerization, because βPL is converted easily to acrylic acids in bulk as described later.

TABLE I
 CH_3COOH -Catalyzed Polymerization of βPL in Bulk^a

Expt. No.	Temp, °C	Time, hr	Conversion, %	
			Polymer insoluble in CH_3OH	Residue after evaporation
G58-4	60	48	0	—
G58-11	"	144	6.1	—
G28-8	80	24	4.2	5.6 ^b
G28-9	120	5	9.3	14.3

^a βPL 3 cc, CH_3COOH 3.1×10^{-5} mole, *in vacuo*.

^b $[\eta]$ in CHCl_3 at $35^\circ\text{C} = 0.057$.

TABLE II
 Thermal Polymerization of β PL^a

Polymerization system	Temp, °C	Time, hr	Conversion, %	
			Polymer insoluble in CH ₃ OH	Residue after evaporation
Bulk	60	48	0	3.4
"	"	144	5.3	65.7
"	80	24	3.9	8.5
"	120	5	12.6	29.1
Toluene solution ^a	80	72	0	0.12
"	120	24	0	1.87

^a β PL 1cc, toluene 4 cc, *in vacuo*.

Bulk Polymerization of β PL by Sodium Toluenesulfonate. A plot of time versus conversion curve of bulk polymerization by sodium toluenesulfonate is shown in Figure 1.

The polymerization activity of sodium toluenesulfonate is much higher than that of acetic acid. When β PL was polymerized at 60°C for 49 hr, the conversion was estimated to be ca. 75%.

The degree of polymerization of β PL obtained increases with increasing conversion. This result shows that the polymerization proceeds in a step-

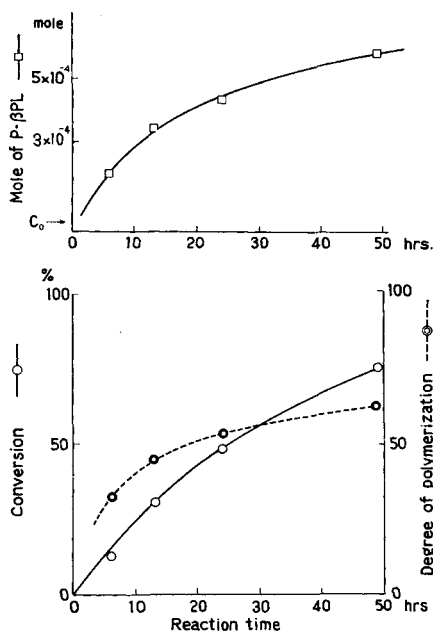


Fig. 1. Bulk polymerization of β PL by $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ catalyst; β PL 3 cc, catalyst 3.1×10^{-5} mole, 60°C, *in vacuo*.

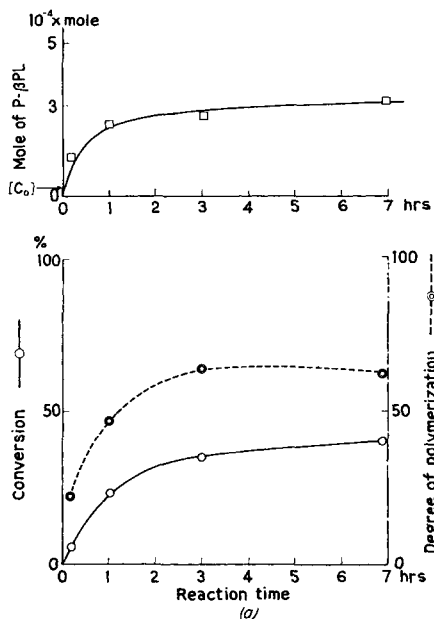


Fig. 2. Bulk polymerization of β PL by $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ catalyst; β PL 3 cc, catalyst 3.1×10^{-5} mole, 60°C , in nitrogen.

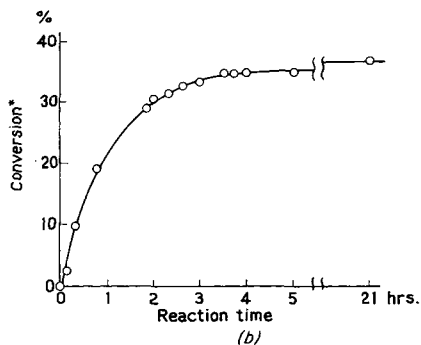


Fig. 3. Polymerization of β PL by $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ in bulk by dilatometry; β PL 3 cc, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ 3.1×10^{-5} mole, 60°C , in N_2 . Conversion was confirmed by analysis of unreacted β PL.

wise fashion. The number of moles of polymer, calculated from the yield of polymer and the degree of polymerization, increases with reaction time up to about 20 times the number of moles of catalyst. These results might be attributable to the occurrence of chain transfer.

Bulk Polymerization of β PL by Toluenesulfonic Acid. A plot of time versus conversion curve for bulk polymerization by toluenesulfonic acid is shown in Figure 2.

Toluenesulfonic acid is dissolved rapidly in β PL and polymerization proceeds in homogeneous system. The rate of cationic polymerization by

toluenesulfonic acid is the same as that of anionic polymerization by sodium acetate, but the degree of polymerization is lower than that by sodium acetate.

The degree of polymerization increases with increasing conversion. The number of molecules of polymer formed in the reaction system increases with reaction time up to 10-fold the number of molecules of catalyst.

The chain transfer reaction predominates in cationic polymerization.

Conversion reaches a saturated value at ca. 35%. This may be explained either by dissolution the low molecular weight polymers in methanol or by a change of active species to less reactive materials.

To determine which is the important factor, β PL was polymerized by using the dilatometric method (Fig. 3). The existence of a large amount of unreacted β PL in the reaction system after the conversion reached a limited value was confirmed. Therefore, the latter explanation is more reasonable.

In propagation of cationic polymerization of β PL, it was concluded by Yamashita^{5,6} that the growing chain end is an oxonium ion and that the lactone ring opens at the acyl-oxygen bond. This conclusion is based on the facts that the product $\gamma_1\gamma_2$ is unity in the copolymerization of β PL and bischloromethyloxetane, the primary carbonium ion is very unstable, and a carbonyl group of the ketene type was detected in styrene- β PL copolymer produced by the cationic mechanism.

On the other hand, in the chain-transfer reaction to monomer in this polymerization, it has been reported^{7,8} that the lactone ring opens at the alkyl-oxygen bond as shown in eq. (1). But the possibility of the chain transfer reaction to monomer by cleavage of the acyl-oxygen bond as shown in eq. (2) should be considered also. The chain end of polymer produced by the reaction (2) should be in a ketene structure. Because ketene is apt to react easily with methanol as precipitant, it must be analyzed before precipitation of the polymer.

The infrared spectrum of the crude product was studied, but the key

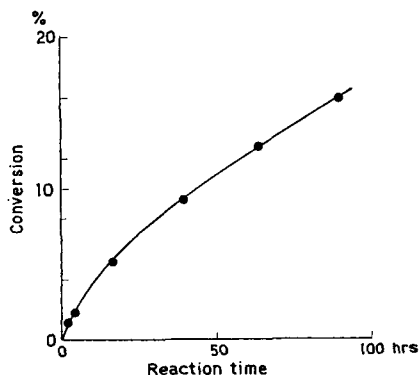
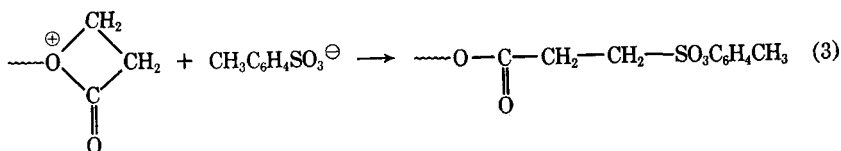
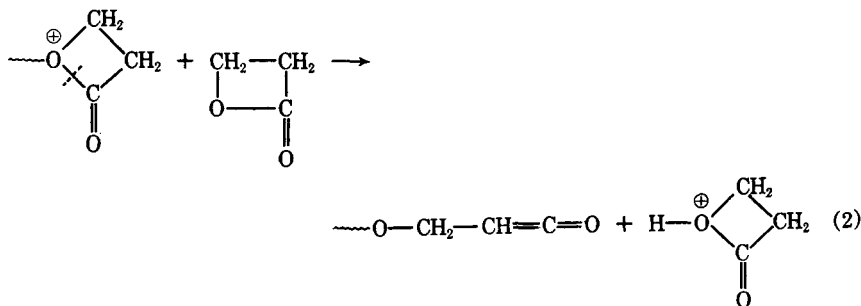
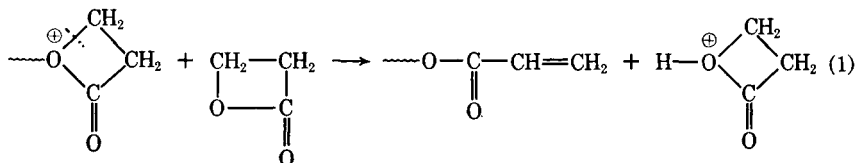


Fig. 4. Polymerization of β PL by $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{CH}_2\text{CH}_3$ in bulk by dilatometry; β PL 3 cc, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{CH}_2\text{CH}_3$ 3.1×10^{-6} mole, 60°C , in N_2 . Conversion was determined by analysis of unreacted β PL.

band of ketene was not observed, possibly on account of the low concentration of chain end.

In chain-transfer reactions as shown in eqs. (1) or (2), the oxonium ion is regenerated, and therefore the rate of polymerization will not decrease. But in the chain-transfer reaction shown in eq. (3), the oxonium ion is not regenerated, and toluenesulfonic ester of low reactivity is produced. The polymerization β PPL by ethyl-*p*-toluenesulfonate is demonstrated in Figure 4.



Summary of Bulk Polymerization. The rate of polymerization (Fig. 5), the relationship between conversion and degree of polymerization (Fig. 6) and the relationship between conversion and number of moles of polymer (Fig. 7) were compared for bulk polymerizations by various catalysts.

These conversions can not be compared strictly because of different solubilities of catalysts; however, it is obvious that the polymerization activity of sodium carboxylate is higher than that of toluenesulfonic acid, and sodium toluenesulfonate has higher activity than acetic acid.

The degree of polymerization observed is smaller than the theoretical value calculated from the molar ratio of reacted monomer to catalyst for all catalysts. These results indicate the existence of the chain transfer reaction to monomer.

The dependence of the degree of polymerization on the nature of catalyst at the fixed conversion is in the order of $\text{CH}_3\text{COONa} > \text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na} \approx \text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} > \text{CH}_3\text{COOH}$.

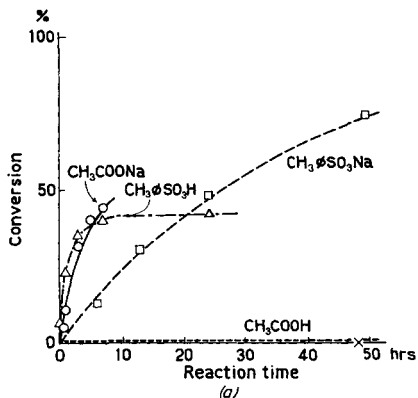


Fig. 5. Comparison of conversions in bulk polymerization of β PL by various catalysts.

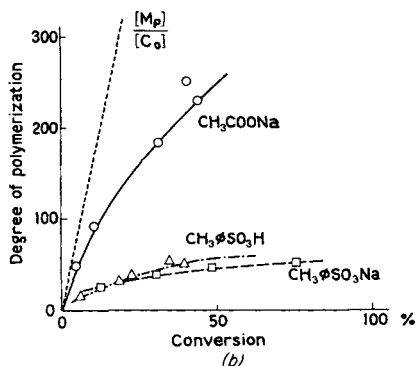


Fig. 6. Relationship between conversion and degree of polymerization in the bulk polymerization of β PL by various catalysts; $[M_p]$ = moles of monomer polymerized, $[Co]$ = moles of catalyst.

The number of moles of polymer formed is 2–3 times that of catalyst in the anionic polymerization by sodium acetate, and 10 times that of catalyst in the cationic polymerization by toluenesulfonic acid. The relationship between the conversion and the number of moles of polymer in the polymerization by sodium toluenesulfonate resembles that of polymerization by toluenesulfonic acid.

Polymerization in Toluene

Polymerization in toluene proceeds heterogeneously and shows an induction period.

Polymerization by Sodium Acetate in Toluene. β PL was polymerized by sodium acetate in toluene. The time-conversion curve is S-shaped because of the presence of induction period (Fig. 8).

The degree of polymerization increases with reaction time in the induction period but does not increase after that. The number of moles of

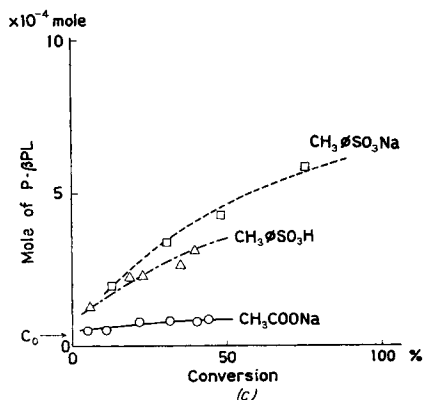


Fig. 7. Relationship between conversion and number of moles of P β PL obtained in the bulk polymerization of β PL by various catalysts.

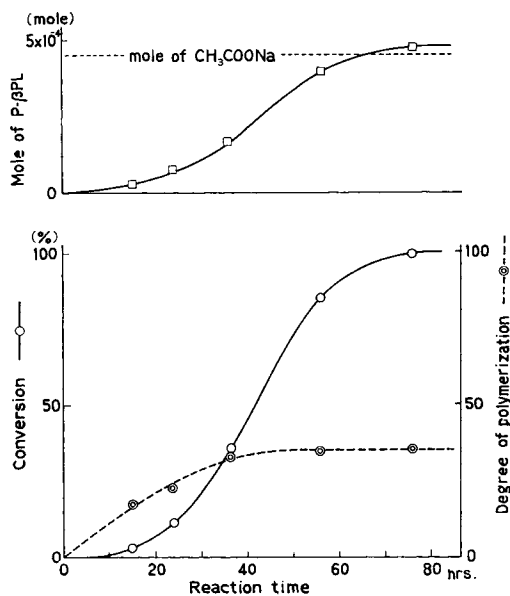


Fig. 8. Polymerization of β PL by CH_3COONa in toluene; β PL 1 cc, toluene 4 cc, CH_3COONa 4.54×10^{-4} mole, 60°C , *in vacuo*.

polymer in the reaction system increases with reaction time, showing a similar tendency as the conversion curve.

The increase in the number of polymer molecules should be attributed to either the chain-transfer reaction or the insolubility of the catalyst.

It was found in our previous paper² that chain transfer does not occur, to any appreciable extent in the polymerization of β PL by sodium carboxylate in toluene. Therefore, it is concluded that the main cause for the increase in the number of molecules of polymer might be the increase of initiating catalyst.

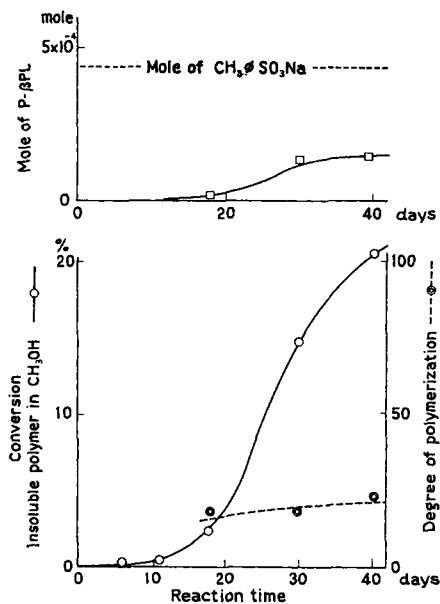


Fig. 9. Polymerization of β PL by $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ in toluene; β PL 1 cc, toluene 4 cc, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ 4.38×10^{-4} mole, 60°C , *in vacuo*.

It seems that β PL is polymerized only at the surface of catalyst in the initial stage, after which polymer is stripped off; fresh catalyst surface then initiates subsequent polymerization.

Polymerization of β PL by Acetic Acid in Toluene. The results of polymerization by acetic acid in toluene and thermal polymerization in toluene are summarized in Tables II and III.

Thermal polymerization occurs more easily in bulk, but hardly occurs in toluene solution.

It is of interest whether the polymerization of β PL by acetic acid proceeds by a cationic or anionic mechanism. Cleavage of the acyl-oxygen bond in β PL is brought about by cationic catalyst and cleavage of the alkyl-oxygen bond is brought about by anionic catalysts.^{5,6,9,10} Therefore, if

TABLE III
 CH_3COOH -Catalyzed Polymerization of β PL in Toluene^a

Expt. No.	Temp. $^\circ\text{C}$	Time, hr	Conversion, %	
			Polymer insoluble in CH_3OH	Residue after evaporation
G58-8	60	48	0	—
G58-12	80	72	0	2.09
G28-7	120	25	0	8.50

^a β PL 1 cc, toluene 4 cc, CH_3COOH 4.54×10^{-4} mole, *in vacuo*.

β PL is polymerized by cationic mechanism, the acid anhydride must exist as an endgroup in the polymer produced. The reaction product obtained with 0.04 mole of β PL and 0.01 mole of CH_3COOH , did not show bands in the infrared spectrum corresponding to acid anhydride, but bands attributable to ester and carboxylic acid were detected.

These results indicate that polymerization of β PL by CH_3COOH proceeds by an anionic mechanism.

Polymerization of β PL by Sodium Toluenesulfonate in Toluene. The rate of polymerization is quite large in the bulk polymerization initiated by sodium toluenesulfonate, but is very small in toluene solution (Fig. 9). An induction period is also observed in this polymerization system. The number of moles of polymer produced in this reaction system is much less than that of catalyst and so it is clear that the initiating efficiency of this catalyst is low owing to its insolubility.

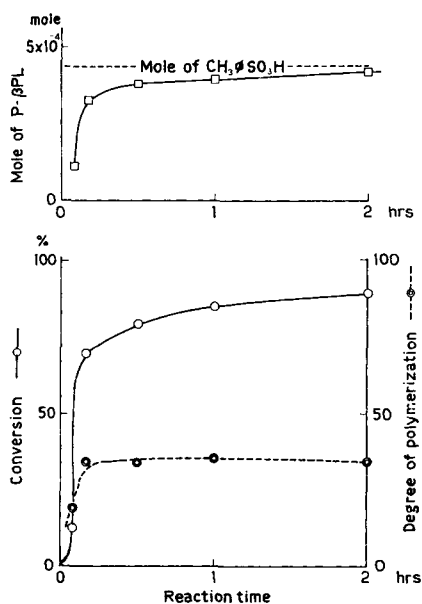


Fig. 10. Polymerization of β PL by $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ in toluene; β PL 1 cc, toluene 4 cc, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ 4.38×10^{-4} mole, 60°C , in nitrogen.

Polymerization of β PL by Toluenesulfonic Acid in Toluene. β PL is polymerized very fast up to ca. 70% yield for 10 min, but after that the rate of polymerization decreases rapidly (Fig. 10). This might result by change of catalyst to *p*-toluene-sulfonic ester by recombination between pair ions.

The degree of polymerization increases with reaction time initially but after that is almost constant.

The number of moles of polymer increases rapidly in the initial period, and at last reaches the same number as that of catalyst.

TABLE IV
Determination of Endgroups of P β PL Obtained with Various Catalysts^a

Expt. No.	Catalyst	Temp, °C	Time, hr	Con- version, %	$[\eta]$	\bar{M}_n	Polymer, mole/g	COOH, mole/g	C=C, mole/g
E30-2	CH ₃ COONa	60	0.5	5.3	0.12	3600	2.8×10^{-4}	2.9×10^{-4}	1.4×10^{-4}
G28-8	CH ₃ COOH	80	24	4.2	0.05	1300	7.4×10^{-4}	7.8×10^{-4}	3.3×10^{-4}
G59-4	CH ₃ C ₆ H ₄ SO ₃ Na	60	49	75.4	0.14	4400	2.2×10^{-4}	2.4×10^{-4}	2.1×10^{-4}
G60-2	CH ₃ C ₆ H ₄ SO ₃ H	60	1	22.8	0.11	3300	3.0×10^{-4}	3.0×10^{-4}	$\sim 0 (< 10^{-6})$

^a β PL, 3 cc, catalyst 3.1×10^{-5} mole, *in vacuo*.

Since toluene does not dissolve both catalyst and the polymer, it may be supposed that the efficiency of initiation will be low.

Summary of Polymerizations in Toluene. The rate of polymerization (Fig. 11), the relationship between conversion and degree of polymerization (Fig. 12), and the relationship between conversion and number of

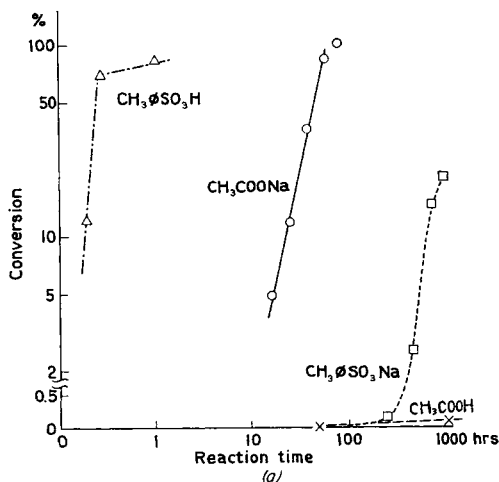


Fig. 11. Comparison of conversions in the polymerization of β PL by various catalysts in toluene.

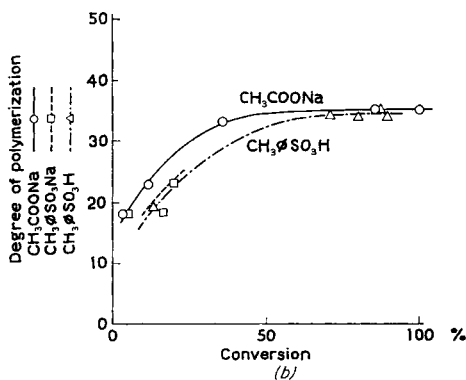


Fig. 12. Relationship between conversion and degree of polymerization in the polymerization of β PL by various catalysts in toluene.

moles of polymer (Fig. 13) are compared for polymerization in toluene by various catalysts.

The order of the rate of polymerization by various catalysts is $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} > \text{CH}_3\text{COONa} > \text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na} > \text{CH}_3\text{COOH}$.

The degree of polymerization at the same conversion does not vary widely.

The number of moles of polymer is lower than that of catalysts added, increases with reaction time, and then approaches the same number as that of the catalyst at 100% conversion.

The mechanism of the chain transfer reaction in the polymerizations cannot be discussed nor compared for the nature of catalysts because of the low efficiency of initiation.

Determination of Endgroups of Polymer (P β PL)

P β PL obtained with various catalysts was purified by reprecipitation and then contents of carboxyl groups and double bonds in the polymer chain end were determined.

In all the polymerizations the number of carboxyl groups in the polymer obtained is almost equal to the number of polymer molecules, calculated as a ratio of polymerization yield and molecular weight of polymer (Table IV). Therefore, one end of the polymer chain is a carboxylic group.

The mole ratios of double bonds to carboxyl groups for the polymers catalyzed by sodium acetate, acetic acid, sodium toluenesulfonate, and toluenesulfonic acid are 50, 40, 90, and 0 mole-%, respectively. These results are

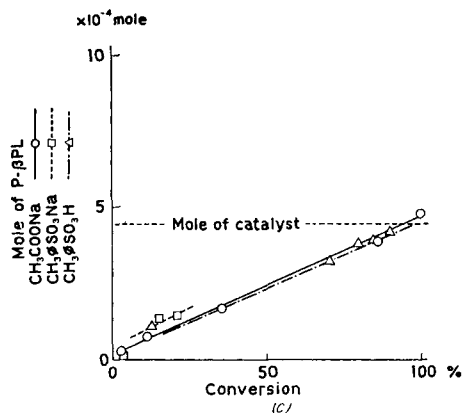


Fig. 13. Relationship between conversion and number of moles of P β PL obtained in the polymerization of β PL by various catalysts in toluene.

illustrated in Figure 14. For the polymer obtained by sodium acetate, about 50% of polymer has an acetyl group and a carboxyl group in each polymer end. The other 50% of polymer, which is produced by chain transfer to monomer, has a double bond and a carboxyl group in each polymer chain end.

In the case of polymerization by acetic acid, similar results were observed. The facts of higher grafting efficiency in the graft copolymerization onto the trunk polymer containing carboxylic acid and the absence of acid anhydride groups might support anionic polymerization by carboxyl anion. In the case of the polymerization by sodium toluenesulfonate, ca. 90% of

polymer molecule has a double bond and a carboxyl group in polymer chain ends.

Acrylic acid which is produced by α -hydrogen transfer reaction of β PL might participate in the initiation reaction in the case of sodium toluene-sulfonate.

In the polymer formed by toluenesulfonic acid, no double bond was found. This polymer chain terminates at one end in a carboxyl group, and at the other end in a hydroxyl group; however analysis of the hydroxyl group in $P\beta$ PL by acetylation cannot be achieved because of decomposition of $P\beta$ PL under the analysis conditions.

Rearrangement of β PL to Acrylic Acid and Thermal Polymerization

Rearrangement of β PL to acrylic acid and thermal polymerization of β PL in bulk and in toluene solution were investigated by the dilatometric method (Fig. 15).

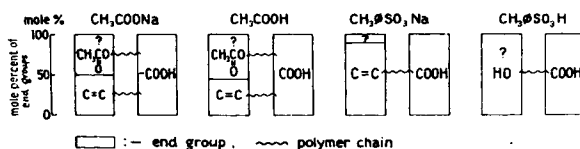


Fig. 14. End groups in $P\beta$ PL obtained with various catalysts.

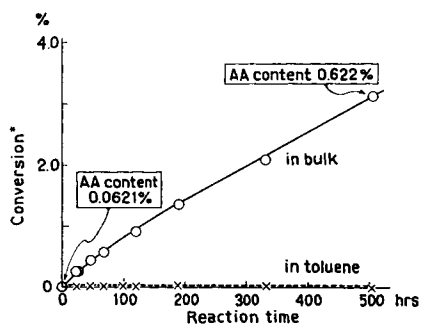


Fig. 15. Thermal polymerization of β PL in toluene or bulk by dilatometry; in bulk: β PL 4 cc, 60°C, in nitrogen; in toluene: β PL 2 cc toluene 8 cc, 60°C, in nitrogen. Conversion was determined by analysis of unreacted monomer.

The conversion of β PL was determined by analysis of unreacted monomer, the yield of acrylic acid was determined by the addition of bromine to the double bond, and the yield of polymer was determined by weighing of methanol-insoluble polymer or evaporation residue.

In the thermal polymerization of β PL at 60°C for 500 hr in bulk, 3.1% of β PL is consumed, and 0.62% of acrylic acid is produced. On the other hand, in the thermal polymerization in toluene under the same conditions, β PL does not change at all.

Effect of Addition of Acrylic Acid onto the Polymerization of β PL in Toluene by Sodium Toluenesulfonate

β PL polymerized by sodium toluenesulfonate has a double bond and a carboxyl group in each polymer end as described above.

Acrylic acid is produced easily from β PL in bulk, but formed with difficulty in toluene. The rate of polymerization by sodium toluenesulfonate in bulk is fast, but the rate of polymerization in toluene is very slow. Acrylic acid formation might be related to the rate of polymerization. Then, the effect of addition of acrylic acid on the polymerization of β PL by sodium toluenesulfonate in toluene was investigated (Fig. 16).

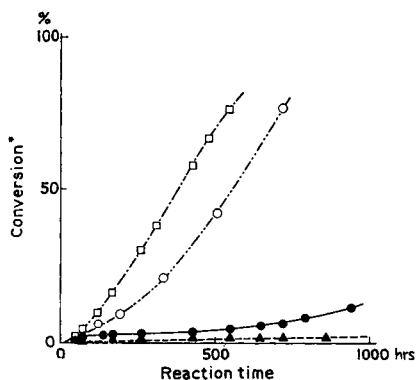


Fig. 16. Polymerization of β PL by $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ in the presence of acrylic acid (AA) in toluene by dilatometry: (●) $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ 4.38×10^{-4} mole; (▲) $\text{CH}_2 = \text{CHCOOH}$ (AA) 21.9×10^{-4} mole; (□) $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ 4.38×10^{-4} mole + AA 21.9×10^{-4} mole; (○) $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ 4.38×10^{-4} mole + AA 4.38×10^{-4} mole. β PL 1 cc, toluene 4 cc, 60°C , in nitrogen. Conversion was determined by analysis of unreacted β PL.

The conversion was determined by analysis of unreacted monomer and was followed dilatometrically.

Conversion for 500 hr in the polymerization by acrylic acid or sodium toluenesulfonate was limited to ca. 1% or 4%, respectively. However, conversion in the polymerization by both sodium toluenesulfonate and equivalent acrylic acid under the same conditions was very high (40%).

DISCUSSION

Polymerization of β PL by Acetic Acid

The possibilities of two polymerization mechanisms are considered in the polymerization by acetic acid as shown in Figure 17.

Both the rate of polymerization and the degree of polymerization are low, because acetic acid dissociates only very slightly, and the growing chain end is apt to recombine with counterion on account of the higher electrophilic nature of cation and higher nucleophilic nature of anion.

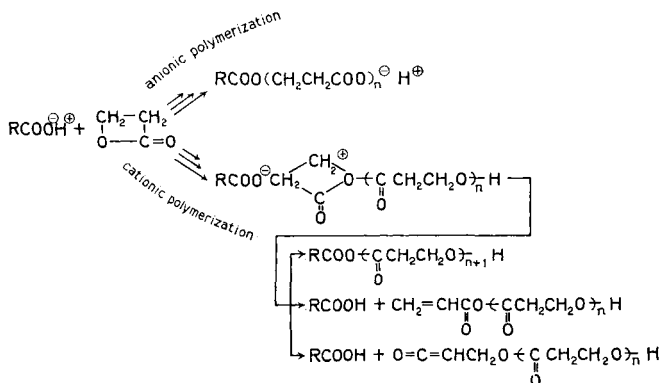


Fig. 17. Possible reaction scheme for polymerization of β PL by RCOOH.

In the bulk polymerization of β PL by acetic acid, the possibility of this initiation and the thermal polymerization which may be initiated by acrylic acid produced by hydrogen transfer reaction of β PL proceed simultaneously, because polymerization activity of acetic acid is similar to that of acrylic acid.

On the other hand, in the polymerization of β PL in toluene by acetic acid, β PL is polymerized by acetic acid without thermal polymerization, because β PL can hardly change to acrylic acid in toluene.

Polymerization of β PL by Sodium Toluenesulfonate

A possible mechanism of polymerization of β PL by sodium toluenesulfonic acid is shown in Figure 18. Gresham et al.¹¹ have reported that sodium β -chloropropionate is produced by the reaction of β PL with sodium chloride. If β PL reacts with sodium toluenesulfonate in the same manner as with sodium chloride, sodium β -toluene-sulfoxypropionate will be produced (reaction 1 in Fig. 18).

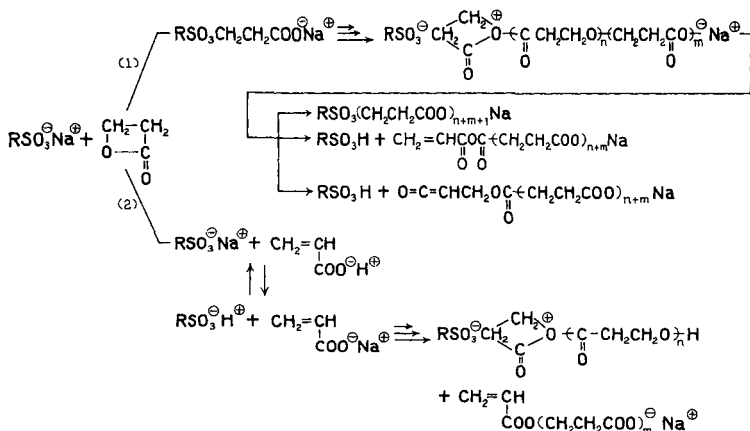


Fig. 18. Possible reaction scheme for polymerization of β PL by RSO_3Na .

This active product has both a cationic active site (sulfonic ester bond) and anionic active site (sodium carboxyl group) in one molecule.

Another possible mechanism was proposed, that is, β PL is polymerized by toluenesulfonic acid and sodium acrylate which are produced by cation exchange between sodium toluenesulfonate and acrylic acid (reaction 2 in Fig. 18).

Polymerization Mechanism of β PL by Toluenesulfonic Acid

Toluenesulfonic acid consists of a cation of higher electrophilicity and an anion of lower nucleophilicity and is a typical cationic catalyst.

The three termination reactions were proposed as shown in eqs. (1)–(3). Toluenesulfonic acid is regenerated by termination processes such as eqs. (1) and (2), and the polymerization is initiated by these regenerated catalyst. The presence of these termination reactions is shown by the fact that the number of moles of polymer increases with reaction time up to about 10 times that of the number of catalyst molecules (Fig. 2).

The limited nature of conversion was concluded to be due to change of the growing chain end and to toluenesulfonic ester as shown at eq. (3).

CONCLUSION

The polymerization behavior with neutral catalysts was compared to that with cationic and anionic catalysts.

The degree of polymerization in bulk increases in the order: $\text{CH}_3\text{COONa} > \text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} \approx \text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na} > \text{CH}_3\text{COOH}$.

The number of moles of polymer obtained in bulk by various catalysts is larger than that of catalyst, and this result means the existence of the chain transfer reaction.

Chain transfer rarely occurs in the polymerization with sodium acetate, but frequent chain transfer occurs in the polymerization by catalyst such as CH_3COOH , $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$.

The polymers obtained with CH_3COONa or CH_3COOH contain fragments of catalyst, therefore it was supposed that β PL is polymerized by these catalysts by an anionic mechanism. On the other hand, the polymers obtained with $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ or $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ contain almost no catalyst fragments.

The polymerization by $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ undoubtedly proceeds by a cationic mechanism, but the mode of polymerization by $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ cannot be determined conclusively; the two possible mechanisms were proposed, as shown in Figure 18.

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