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Preparation of Block Copolymer of ε-Caprolactone with Living Polystyrene

Koji NOBUTOKI and Hiroshi SUMITOMO

Department of Chemical Technology, Faculty of Engineering, Osaka University, Higashinoda, Miyakojima, Osaka

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ε-Caprolactone was polymerized by using living polystyrene prepared by means of an anionic polymerization technique. A gross polymer was elution-fractionated into four fractions which were methanol-soluble low-molecular-weight polyester, high-molecular-weight polyester, a small amount of polystyrene and polystyrene-polyester block copolymer. Both yields and molecular weights of block copolymers were observed to be higher in benzene than in tetrahydrofuran. Formation of block copolymers was concluded from the results of an elementary- and infrared analyses and turbidometry. Polymerization mechanism of ε-caprolactone is discussed.

Newer preparative methods of block and graft copolymers through anionic living polymerizations have been recently developed.[1–7] An attempt was made in a previous paper[4] to prepare a new class of polymers containing silicone in the main chain by the polycondensation between di-sodium compound of α-methyl styrene tetramer and dimethyl dichlorosilane.

Although considerable attention has been paid to anionic polymerizations of lactones,[8] little information has yet been given as to those initiated by living polymer anions.

In the present paper, is described the polymerization of ε-caprolactone initiated by living polystyrene, leading to the formation of B–A–B type block copolymer.

Experimental

Materials. Styrene (St) was freshly distilled at a reduced pressure after drying over calcium hydride. Tetrahydrofuran (THF) was distilled after refluxing with sodium naphthalene. Benzene was distilled after drying with sodium.

ε-Caprolactone (CL), bp 108.0—109.0°C/10 mmHg was distilled at a reduced pressure from calcium hydride. Monomer and solvents were directly introduced into polymerization vessels by distillations from calcium hydride (in the case of monomer) or from sodium-naphthalene (solvents) after repeating evacuations under freezings and thawings in a vacuum line (10^{-6} mmHg).

Polymerization. General experimental techniques of a homogeneous anionic polymerization developed by Szwarc[9] and by Morton *et al.*[10] were employed in the present investigation.

Preparation of Living Polystyrene. A sketch of the apparatus for the preparation of living polystyrene appears in Fig. 1.

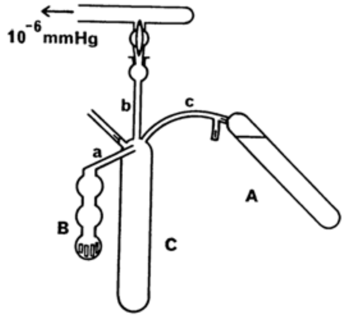

Fig. 1. Apparatus for the preparation of a living polymer.

Ampule A with a break seal containing the solution of St in THF prepared *in vacuo* and ampule B containing sodium metal were attached to ampule C, and then this equipment was evacuated. Sodium was vaporized by heating and deposited as a mirror on the wall of C. B was cut away at *a* and C at *b*.

The solution of St in THF was transfered into C by crushing the break seal in A. The colorless solution changed immediately to dark red one. After being allowed to stand for a fixed time at a constant temperature, A was sealed off at *c*. The solution of living polystyrene in THF thus prepared was divided into several ampules under vacuum to be used in the following reactions.

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1) M. Morton, T. E. Helminiak, S. D. Gadkary and F. Bueche, *J. Polymer Sci.*, **57**, 471 (1962).

2) G. Finaz, Y. Gallot, J. Parrod and R. Rempp, *ibid.*, **58**, 1363 (1962).

3) T. A. Orofino and F. Wenger, *J. Phys. Chem.*, **67**, 566 (1963).

4) H. Sumitomo, K. Nobutoki and Y. Hachihama, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 1966 (1964).

5) M. Morton, A. A. Rembaum and E. E. Bostick, *J. Appl. Polymer Sci.*, **8**, 2707 (1964).

6) R. P. Zelinski and C. F. Wofford, *J. Polymer Sci.*, **A3**, 93 (1965).

7) T. Altares, Jr., D. P. Wyman, V. R. Allen and K. Meyersen, *ibid.*, **A3**, 4131 (1965).

8) H. Cherdron, H. Ohse and F. Korte, *Makromol. Chem.*, **56**, 179, 187 (1962).

9) M. Szwarc, *J. Am. Chem. Soc.*, **78**, 2656 (1956).

10) M. Morton, R. Milkovich, D. B. McIntyre and L. J. Bradley, *J. Polymer Sci.*, **A1**, 443 (1963).

Polymerization of ε-Caprolactone with Living Polystyrene. The flask F was equipped with the ampule D, in which a lactone solution was charged *in vacuo,* and the ampule E containing a living polystyrene solution, as seen in Fig. 2. After the system was evacuated, the flask F was sealed off at *d* and then the break seal of E was crushed. A living polystyrene solution transfered into F was kept at a constant temperature. To the living polystyrene solution a lactone solution was added from D after breaking the seal. Termination of the reaction was attained by the addition of 1/10 N hydrochloric acid solution. After the solvent was distilled off under a reduced pressure, the product was again dissolved in benzene. The solution was washed with water to remove an inorganic by-product. The gross polymer was recovered and purified by means of reprecipitation and freezing-drying methods.

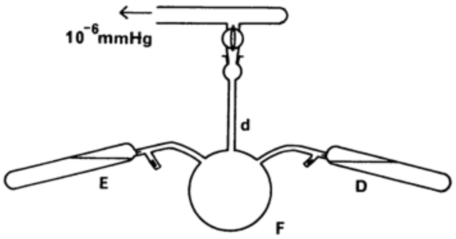

Fig. 2. Apparatus for the polymerization of a lactone with use of a living polymer.

Solution Viscosity. Viscosities of samples in cyclohexane or chloroform were measured using an Ubbelohde-type viscometer in three to four concentrations, *c*, below about 1 g/100 m*l*. Intrinsic viscosities, [η], were determined by the extrapolation of curves of η_{sp}/c *vs.* c to $c=0$.

Infrared Absorption Spectra. Infrared spectra were measured using the film method.

Molecular Weight of Block Copolymer. Molecular weight of polystyrene was calculated from the molecular weight - intrinsic viscosity relationship.[11] That of poly-ε-caprolactone part was calculated from the result of the elemental analysis and the molecular weight of polystyrene part.

Results and Discussion

Preparation of Living Polystyrene. Table 1 shows the results of the polymerization of styrene (St) with sodium in THF. The polymer yields were quantitative. Molecular weights of the polymers were calculated from the following equation[11] using viscosity data.

$$[\eta]_\theta = 8.5\times10^{-4}\,\mathrm{M}^{0.5} \text{ (cyclohexane, 34.5°C)}$$

Polymerization of ε-Caprolactone with Living Polystyrene. The results of the polymerization of ε-caprolactone (CL) using living PSt prepared at −78°C are listed in Table 2.

TABLE 1. PREPARATION OF LIVING POLYSTYRENE

Expt. No.	St g	St-THF solution m*l*	Na g	Temp. °C	Time hr	Concn. of living PSt×10^4 a) mol/*l*	MW 10^{-4} b)	[η]c)
3	17.25	228.0	1.32	−78	6	6.34	13.6	0.66
4	13.03	226.4	2.70	−78	6	4.68	10.2	0.47

a) Conversion, 100%.
b) Calculated using $[\eta]_\theta=8.5\times10^{-4}\,\mathrm{M}^{0.5}$ (cyclohexane, 34.5°C).
c) Chloroform, 30°C, 100 m*l*/g

TABLE 2. POLYMERIZATION OF ε-CAPROLACTONE WITH LIVING POLYSTYRENE AT ROOM TEMPERATURE

Expt. No.	Living PSt −THF soln. m*l*	Living PSt g	CL g	Solvent			Time min	Yield g	Convn. %	Fr. 2 g	Fr. 3 g	Fr. 4 g	[η] of Fr. 3	[η] of Fr. 4
				Ben-zene m*l*	THF m*l*	THF vol%								
11	10.0	0.61	3.23	45.0	0	0	30	3.75	97.7	0.02	1.56	0.92	1.62	1.54b)
12	7.4	0.59	2.56	24.0	7.4	23.6	30	2.33a)	74.0	0.05	1.35	0.82	2.40	2.22c)
13	10.0	0.61	3.23	33.8	11.2	25.0	30	3.79	98.7	0.01	2.21	0.73	1.23	1.36b)
14	10.0	0.61	3.23	22.5	22.5	50.0	30	3.71	96.6	0.05	2.35	0.60	1.01	1.20b)
15	10.0	0.61	3.23	11.3	33.7	75.0	30	3.61	94.0	0.04	2.10	0.70	—	0.99b)
16	10.0	0.61	3.23	0	45.0	100	30	3.59	93.5	0.08	1.72	0.64	—	—
17	10.0	0.61	3.23	0	45.0	100	30	2.35a)	61.2	0.05	0.97	0.67	0.62	0.90b)

a) Precipitated in benzene-methanol system.
b, c) Intrinsic viscosities of parent polystyrenes were as follows:
b) 0.47 and c) 0.66 (in chloroform, 30°C, 100 m*l*/g).

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11) T. Altares, Jr., D. P. Wyman and V. R. Allen, *J. Polymer Sci.,* **A2**, 4533 (1964); **A3**, 2719 (1965).

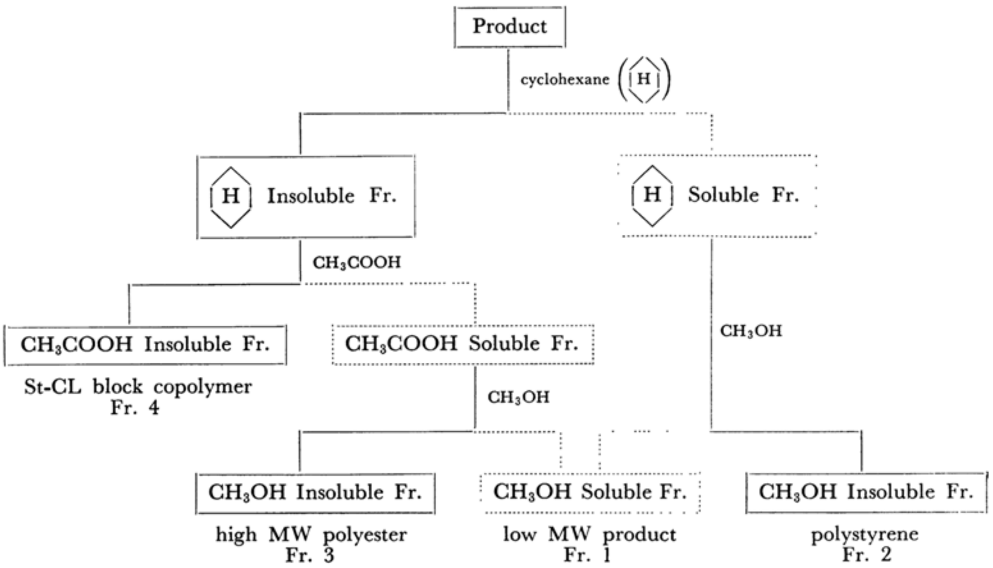

Fig. 3. An elution-fractionation scheme for the product in ε-caprolactone-living polystyrene system.
——, Insoluble fraction ……, Soluble fraction

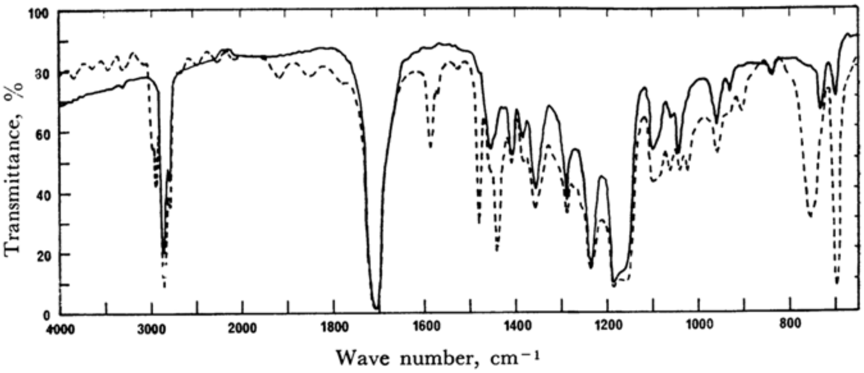

Fig. 4. Infrared absorption spectra of the block copolymer and the homo-polyester obtained in living PSt-CL system (film).
——, High molecular weight homo-polyester (Fr. 3) ……, Block copolymer (Fr. 4)

The low conversions in runs 12 and 17 may be attributed to the loss of low molecular weight products during the process of reprecipitation using benzene-methanol system.

A gross polymer obtained here was elution-fractionated using cyclohexane and acetic acid as solvents into four fractions, as shown in Fig. 3. From infrared analysis fraction 1, 2, 3 and 4 were found, respectively, to be low molecular weight CL polymer, a small amount of PSt, high molecular weight polyester containing a slight amount of PSt unit and PSt-polyester block copolymer. The yields and intrinsic viscosities of these fractions are included in Table 2.

In Fig. 4 are illustrated infrared absorption spectra of fractions 3 and 4. Fraction 3 is assumed from the spectrum to consist of virtually homo-polyester, in which the absorption bands characteristic of an ester group of poly-ε-caprolactone mainly appear, together with the extremely weak bands of St unit. The spectrum of fraction 4 shows that it contains solely the PSt-CL block copolymer.

An attempt was made to estimate the composition and average molecular size for one of the block copolymers. The result obtained for the Fr. 4 polymer of run 12 is summarized in Table 3.

The influence of the solvent composition on polymer yields is represented in Fig. 5. It may be suggested that the yield of block copolymer (Fr. 4) was slightly higher in the range of lower content of THF than of higher content and that the yield of low molecular weight product (Fr. 1) tended to increase in the range of higher THF

Table 3. Evaluation of the composition and molecular weight for PSt-CL block copolymer (Fr. 4 obtained in run 12)

Copolymer		PSt part				PCL part		
$[\eta]$ a)	MW $\times 10^{-4}$ b)	Content c)		$[\eta]$ a,d)	MW $\times 10^{-4}$ d)	Content, c)		MW $\times 10^{-4}$ e)
		mol%	wt%			mol%	wt%	
2.22	22.2	63.44	61.31	0.66	13.6	36.56	38.69	8.6

a) Chloroform, 30.0°C.
b) Sum of the molecular weights of polystyrene part and of poly-ε-caprolactone part.
c) Calculated from the result of the elemental analysis.
d) Data for the parent polystyrene (Table 1).
e) Deduced from the composition of the copolymer and the molecular weight of polystyrene part.

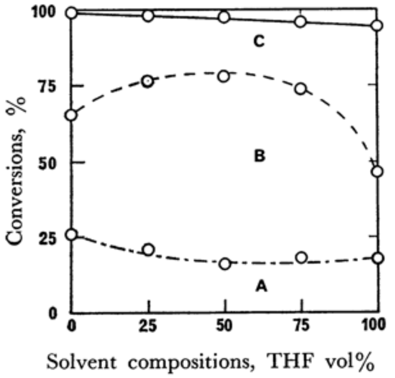

Fig. 5. Effects of solvent compositions on conversions of ε-caprolactone polymerized by living polystyrene.
Region A, St-CL block copolymer (Fr. 4)
Region B, high molecular weight polyester (Fr. 3)
Region C, low molecular weight product (Fr. 1)

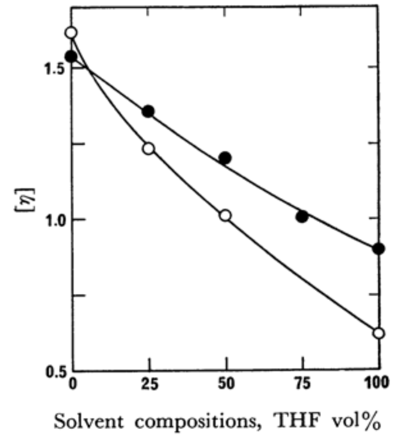

Fig. 6. Effects of solvent compositions on intrinsic viscosities of products in PSt-CL system.
●, St-CL block copolymer (Fr. 4)
○, High molecular weight polyester (Fr. 3)

content. The intrinsic viscosities of Frs. 3 and 4 decreased with THF contents in the polymerization medium (in Fig. 6). It is conceivable from these facts that the molecular weights of the products decrease with increasing the polarity of the medium.

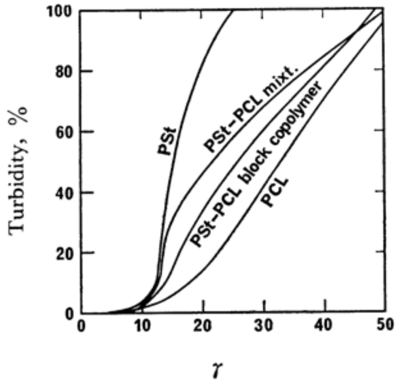

Fig. 7. Turbidometric titration curves of block copolymer, polymer mixture and homopolymer.
Solvent, Tetrahydrofuran
Precipitant, methanol

Figure 7 shows the results of turbidometric titrations of the solutions of PSt, PCL, their mixture and the block copolymer in tetrahydrofuran using methanol as a precipitant. In Table 4 are listed γ values, (volume of precipitant/total volume of solvent and precipitant) × 100, for PSt and PCL in various solvent-precipitant systems which have been determined by means of the turbidometry. It appears that the solubility of PCL is larger in benzene than in THF.

Table 4. The results of turbidometric titrations of polystyrene and poly-ε-caprolactone solutions

Solvent	Precipitant	γ a)	
		PSt	PCL
Benzene	Methanol	29	59
THF	Methanol	44	52.5
THF	Water	12.5	18

a) (volume of precipitant/total volume of solvent and precipitant) × 100

Table 5. Polymerization of ε-caprolactone with sodium ethylate

CL g	THF m*l*	C_2H_5ONa mg	Temp.	Time hr	Yield g	Convn. %	Methanol soluble fraction		Methanol insoluble fraction		Molecular weight of methanol soluble fraction	
							g	[η]	g	[η]	VPO method[b]	Cryoscopy[c]
3.23	44	10.1	r.t.[a]	1	3.18	98.5	1.17	0.04	1.90	0.55	455.7	445.2

a) Room temperature.
b) Using Mechrolab Model 302 Vapor Pressure Osmometer.
c) In benzene.

Polymerization of ε-Caprolactone using Sodium Ethylate. It was observed that the polymerization of CL was able to be initiated with sodium ethylate at room temperature (Table 5), but not with sodium propionate. This fact suggests that the active species in the propagation may be alcoholate anions.

Mechanism of Polymerization of ε-Caprolactone. It seems probable from the results obtained above that the polymerization of CL is started by the cleavage of the bond between a carbonyl group and oxygen of the monomer. The active ends during the propagation are thought to be alcoholate anions. Namely, CL propagates also through the carbonyl carbon-oxygen fissions.

Chain Transfer to Monomer. CL monomer itself does not easily polymerize even when it is heated to its boiling temperature. It has been also observed that there is no possibility of any initiation of the polymerization caused by free sodium metal or sodium hydroxide which might be involved as impurities in living polymer solutions. Ladacki[12] showed recently that living polymers were very stable for a long period. It may be probable from these facts that the low molecular weight polymer of CL in the present system might come from some chain transfer to monomer.

It would be interesting to note that the observations in the present reaction systems could be interpreted by assuming some combinations of the influences of (i) solubilities of the living polymers, the monomer and the resulting polymers in the reaction media, (ii) molecular weights of the living polymers, (iii) solvations, (iv) polarities of solvents and (v) chain transfers.

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12) M. Ladacki, *J. Appl. Polymer Sci.*, **9**, 1561 (1965).