Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Niwa, Masazo , Akahori, Masahiko and Nishizawa, Shigetoshi(1987) 'Synthesis of Graft Polymers by Copolymerization of Macromonomer. III. Preparation and Copolymerization of Styrene-Terminated Poly(Oxyethylene) Macromonomer', Journal of Macromolecular Science, Part A, 24: 12, 1423 — 1444

To link to this Article: DOI: 10.1080/00222338708078151

URL: http://dx.doi.org/10.1080/00222338708078151

J. MACROMOL. SCI.—CHEM., A24(12), pp. 1423-1444 (1987)

SYNTHESIS OF GRAFT POLYMERS BY COPOLYMERIZATION OF MACROMONOMER. III. PREPARATION AND COPOLYMERIZATION OF STYRENE-TERMINATED POLY(OXYETHYLENE) MACROMONOMER

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ABSTRACT

Styrene-terminated poly(oxyethylene) macromonomers (SOE) with narrow molecular weight distribution and quantitative styrene monofunctionality were synthesized. In homopolymerization of SOE, conversion of monomer to polymer was shown to be low in spite of high consumption of the vinyl groups of the SOE molecules. Free-radical copolymerization of the macromonomer with methyl methacrylate and styrene occurred smoothly, as opposed to homopolymerization. Cumulative copolymer composition and total conversion were determined from the conversions of macromonomer and comonomer (by weight changes) and by proton NMR of the copolymer. The monomer reactivity ratios were found to be $r_a = 0.06$ and $r_b = 2.0$ for the copolymerization of SOE macromonomer (a) with methyl methacrylate (b). In this case the macromonomer exhibited considerably lower reactivity than predicted from its low molecular weight model compound. The monomer reactivity ratios estimated for SOE and styrene were $r_a = 0.86$ and $r_b = 1.20$. The reactivity of SOE was comparable to, but somewhat lower than, styrene. The graft copolymers were used as activators in the halogen displacement reaction, and it was found that their catalytic activity depends on copolymer composition and chemical structure.

INTRODUCTION

Graft polymers possess physical properties and functional activities that depend on the chemical composition and the chain length of the macromonomer, and the kinds of comonomer in the product. From the viewpoint of molecular design of graft polymers, there have been many reports on copolymerizations of macromonomers with suitable comonomers [1-3]. We recently reported on the syntheses of macromonomers with various types of main-chain structures with unsaturated end groups [4]. It is important to determine the copolymerization reactivities of these macromonomers in order to design well-defined graft polymers. We have published a paper about the reactivity ratios for free-radical copolymerizations of these macromonomers with vinyl monomers and found that styrene-terminated poly(2-acetoxyethyl methacrylate) macromonomer exhibited low reactivity compared to the other macromonomers [5].

This article concerns the reactivities in homopolymerization of styrene-terminated poly(oxyethylene) macromonomer (SOE) and of its copolymerization to afford copolymer with hydrophilic graft chains. In addition, the effects of chemical composition of well-defined graft polymers on the catalytic activity of the halogen exchange reaction are also described.

EXPERIMENTAL

Materials

Sodium poly(oxyethylene) glycol monomethyl ethers (*n* 46 and 120) were obtained from Nihon Shokubai Kagaku. Chloromethylstyrene, methyl methacrylate, styrene, and 1-bromooctane were purified by distillation under reduced pressure. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Solvents were obtained commercially and used after being purified by the usual means. Sodium iodide was used without further purification.

SOE macromonomer was prepared by the reaction in alkaline medium of chloromethylstyrene and sodium poly(oxyethylene) glycol monomethyl ether [6] with tetrabutylammonium hydrogen sulfate as phase-transfer catalyst. The reaction was run for 48 h at room temperature. The organic phase was separated, washed with water, and acidified with a few drops of dilute aqueous hydrochloric acid. Purification was performed by precipitating a dichloromethane solutions into petroleum ether. The macromonomer was freeze-dried under vacuum. These SOE macromonomers were characterized by proton NMR and UV spectrometry.

Measurements

Gel-permeation chromatograms (GPC) were obtained on a Shimadzu high-performance liquid chromatograph (Model LC-3A) equipped with three columns (HSG-15, HSG-30, and HSG-50). The products were detected with a dual differential refractometer (Model Shodex RI SE-11) and UV spectrophotometer (Model SPD-2A). The flow of tetrahydrofuran was maintained at 1 mL/min at 40°C. The elution volume-molecular weight calibration curve was determined with standard polystyrene samples.

Proton NMR spectra were recorded on a 400 MHz instrument, JOEL JNM-GX400 FT NMR spectrometer, using deuterochloroform as solvent. Carbon-13 NMR spectra were also recorded with the instrument. Tetramethylsilane was used as the internal standard in all cases.

The UV spectra were recorded with a Shimadzu UV-120 spectrophotometer, using tetrahydrofuran solutions.

GLC analysis were carried out on a Shimadzu Model GC8-AIT instrument, equipped with a TCD. The column was Silicone GE SF-96 on Shimalite W at 160°C.

Polymerization and Copolymerization of Macromonomer

Homopolymerization and copolymerization of SOE were carried out in a sealed glass ampule at 50 and 80°C. SOE macromonomer, comonomer, solvent, and 1.0 mol% AIBN (based on total monomers) were charged into a Pyrex tube and subjected to five freeze-thaw cycles for degassing. The tube was sealed under vacuum and placed in a thermostated bath for the desired period of time. The ampule was then removed from the bath, allowed to cool to -20°C, and then cautiously opened. The reaction mixture was poured into a large amount of petroleum ether. The polymer was purified by reprecipitation.

Products of the homopolymerization were analyzed periodically by GPC. For copolymerization, the reprecipitation was repeated several times from dichloromethane solution into petroleum ether to remove the unreacted comonomer and the initiator. About 10% of the product after reprecipitation was dried in vacuum to constant weight and the total weight W_1 of product dried was obtained. To remove the unreacted SOE, the reprecipitation was repeated several times from dichloromethane solution into water, and then the polymer was dried in vacuum to constant weight and was weighed (W_2).

The chemical composition of the copolymers was determined by proton NMR analysis and also by use of the weights W_1 and W_2.

Evaluation of Catalytic Activity of the Graft Copolymer

To evaluate of catalytic activities of the graft copolymers, we used the halogen-exchange reaction of 1-bromooctane with sodium iodide. The reaction catalyzed by the graft copolymers was carried out at 80°C in toluene. In a typical run a 50-mL three-necked flask was charged with the catalyst, a 0.80 mol/L solution of sodium iodide, and a 0.160 mol/L solution of tetralin (internal standard for GLC) in toluene. After the mixture was stirred mechanically at 600 rpm for 15 min, 1-bromooctane was added at zero time, and samples of the organic phase were analyzed periodically by GLC.

RESULTS AND DISCUSSION

In this study we first prepared and characterized SOE macromonomer by reacting chloromethylstyrene with sodium methoxy poly(oxyethylene) glycol prepolymer. The refractive index GPC curve of SOE-II is almost the same as that for the prepolymer (Fig. 1) but the UV absorption of the prepolymer, which is due to the vinylbenzyloxyl groups, is negligible compared with that of SOE-II. Therefore, the amount of vinylbenzyloxyl groups was determined by using the molar extinction coefficient ($\epsilon = 1.59 \times 10^4$ L/(mol·cm)) from the literature [7].

Number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and contents of vinyl groups of macromonomer are summarized in Table 1. The $\bar{M}_n$ of SOE is consistent with the value calculated from the $\bar{M}_n$ of the prepolymer and the reaction scheme. The number of vinylbenzyloxyl units per macromonomer molecule, N_u, is found to be approximately unity within the limits of experimental error. It was also confirmed by proton NMR that the SOE macromonomers have one vinylbenzyloxyl group per molecule.

Homopolymerization of SOE

Benzene and dioxane were used to study the effects of solvents on the reactivity of SOE in homopolymerization. The UV GPC curve of homopolymerized SOE shows that the concentration of vinylbenzyloxyl groups decreased with polymerization time (Fig. 2). The consumption of vinylbenzyloxyl groups was greater than the amount of homopolymer formed as observed by RI detector. In Fig. 3 the homopolymer produced in benzene was somewhat less than that in dioxane. However, the homopolymerization of a macromonomer is difficult: homopolymer was obtained only after a long time. We ascribe this to the bulkiness of the macromonomer chain and a

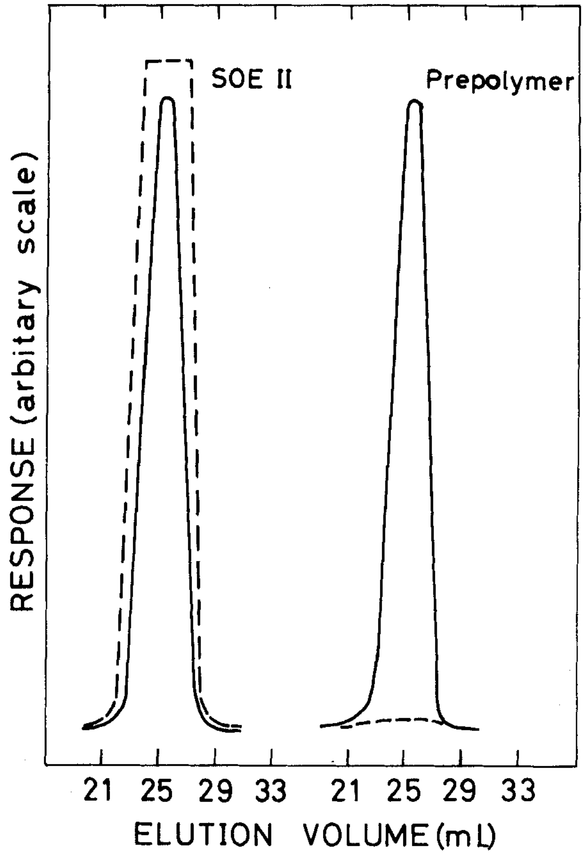

FIG. 1. GPC traces of SOE-II macromonomer and its raw prepolymers. Recorded by RI detector and UV detector (at 252 nm) represented by solid line and broken lines, respectively.

consequent lack of accessibility of the active site. It seems that primary radical termination dominates in the polymerization.

Homopolymers had molecular weights from 46 000 to 55 000. The molecular weights of poly(SOE) obtained in dioxane were somewhat lower than those obtained in benzene. Degrees of polymerization were calculated by using the $\bar{M}_n$ of the respective macromonomers. The degrees of polymerization of the poly(SOE) obtained were strikingly low (21-25). Comparative

TABLE 1. Characteristics of the Styrene-Terminated Poly(Oxyethylene) Macromonomer (SOE)

Polymer	Molecular weight[a]		$\bar{M}_w/\bar{M}_n$	Unsaturation,[b] mmol/g	N_u[c]	
	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$				
SOE-I	6.02	7.64	1.3	0.153	0.92[d]	0.92[e]
Prepolymer-I	5.90	7.47	1.3			
SOE-II	2.14	2.57	1.2	0.448	0.96[d]	0.94[e]
Prepolymer-II	1.89	2.12	1.1			

[a] Calculated from GPC data with polystyrene calibration.

[b] Calculated by using $\epsilon_{max} = 1.59 \times 10^4$ L/(mol·cm) at $\lambda_{max} = 252$ nm, from Ref. 7.

[c] Number of vinylbenzyloxyl groups per macromonomer molecule.

[d] Calculated from $\bar{M}_n$ and content of unsaturation.

[e] Calculated from NMR intensity ratio of oxyethylene proton peak to benzene ring proton peak.

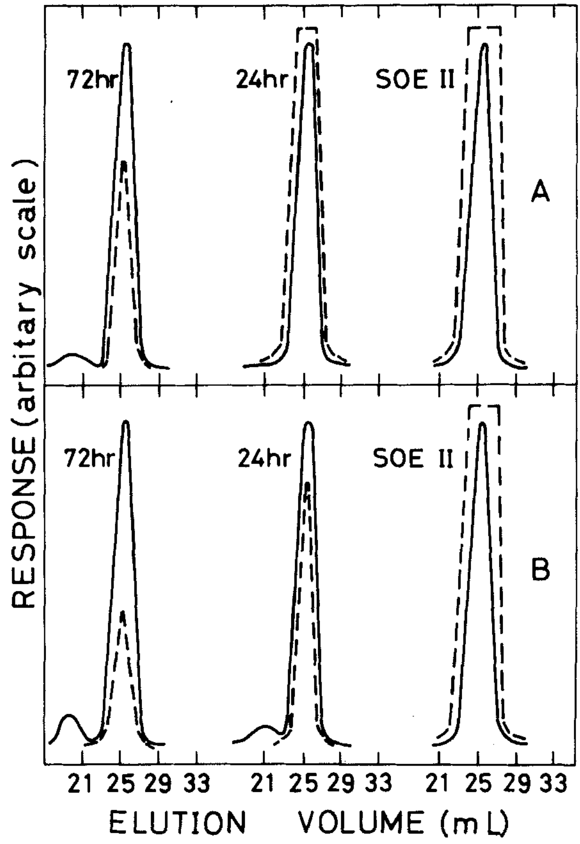

FIG. 2. GPC traces of the SOE-II and that of the products of homopolymerization at 50°C in benzene (A) and in dioxane (B). [SOE] = 0.2 mol/L, [AIBN] = 2.0 mmol/L, polymerization time 24 h. Solid lines RI, dashed lines UV.

experiments with styrene, as a low molecular weight model compound, under the same conditions lead to a much higher degree of polymerization (128).

Copolymerization of SOE Macromonomer

Copolymerizations of SOE with methyl methacrylate and styrene (in benzene at 80°C with AIBN) proceeded smoothly, in contrast to the homopolym-

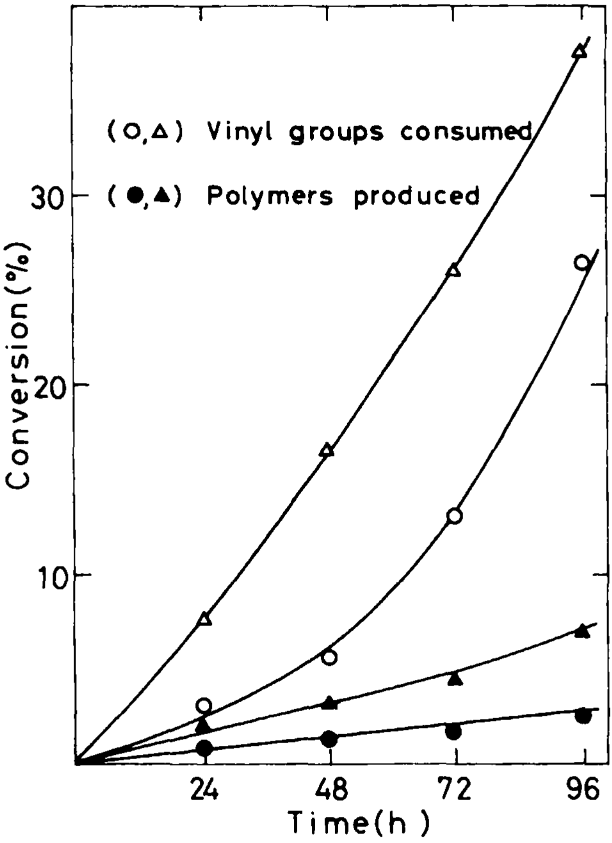

FIG. 3. Plots of the conversion of vinylbenzyloxyl groups consumed and of homopolymer produced versus polymerization time. Solvents: benzene (●) and dioxane (○).

erization. It seems that the main factor is ease of accessibility of the comonomer.

A typical proton NMR spectrum of the copolymer of SOE-II and methyl methacrylate is presented in Fig. 4. Signal A at 6.9-7.3 is due to the aromatic protons in the benzyl groups of the SOE units. The copolymer composition (mole fraction of SOE units, $\bar{F}_a$) was estimated by the intensity ratio of Peak B at 3.6-4.1 due to the oxyethylene protons of the SOE unit to Peak C at

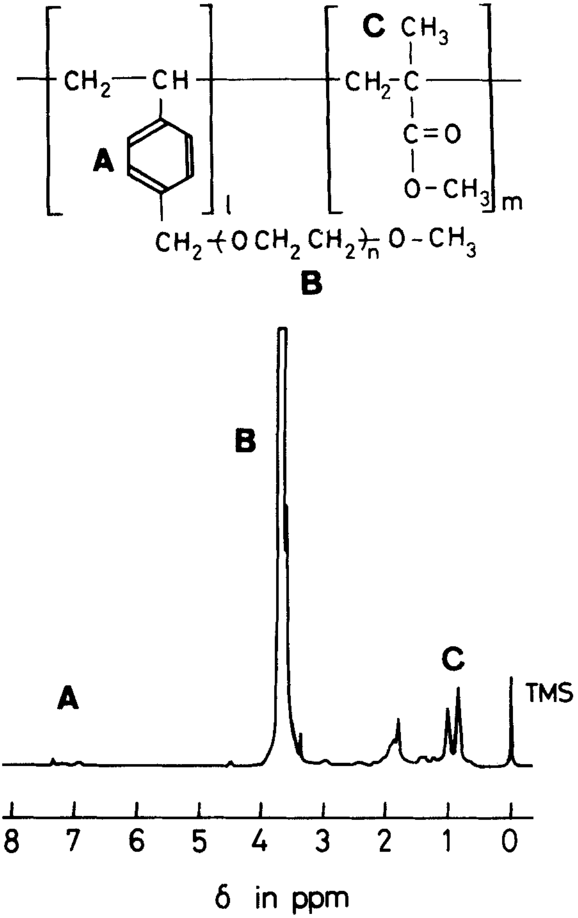

FIG. 4. 400 MHz proton NMR spectrum of the copolymer of SOE-II and methyl methacrylate in deuterochloform.

0.91-1.20 due to α-methyl proton resonances of the methyl methacrylate unit.

The total conversion (weight fraction, X_w) was calculated by Eq. (1), while $\bar{F}_a$ was determined by Eq. (2) from W_1 and W_2.

$$X_w = \frac{x_a W_a + x_b W_b}{W_a + W_b}, \tag{1}$$

$$\bar{F}_a = \frac{x_a W_a/M_a}{(x_a W_a/M_a) + (x_b W_b/M_b)}. \tag{2}$$

where M_a and M_b denote the molecular weights of SOE and comonomer, W_a and W_b denote weights of SOE and comonomer in the feed, and x_a and x_b are conversions (in mole fraction) of SOE and comonomer with $(1 - x_a) = (W_1 - W_2)/W_a$ and $x_b = (W_1 - W_a)/W_b$, respectively.

The results of copolymerization of SOE with methyl methacrylate are shown in Table 2. The mole fractions of SOE in the graft copolymer ($\bar{F}_a$) estimated by proton NMR are in good agreement with those determined from W_1 and W_2.

Figures 5 and 6 show the relationship between cumulative copolymer composition ($\bar{F}_a$) and conversion from experimental results. The proportion of grafts in the copolymer is lower than the proportion of SOE in the feed. In order to compare the reactivities of SOE macromonomer and the model monomer in the copolymerization system, styrene was selected as model monomer. The theoretical $\bar{F}_a$ and conversion curves calculated by using the integral expression for binary copolymerization derived by Alfrey and Goldfinger [9] and the monomer reactivity ratios $r_a = 0.52$ and $r_b = 0.46$ for styrene (a) and methyl methacrylate (b) copolymerization [8] are shown in Fig. 6. All experimental plots are lower than the theoretical (broken) lines at each feed composition.

The monomer reactivity ratios in the SOE-methyl methacrylate system were determined by fitting experimental data to theoretical $\bar{F}_a$-conversion curves plotted from the integral expression. The reactivity ratios estimated were $r_a = 0.06$ and $r_b = 2.0$. These values differ greatly from literature values for styrene-methyl methacrylate and indicate that the reactivity of SOE is markedly lower than that of styrene. This seems to be related to the hydrophilic chain of SOE since the deviation is much larger than that for the styrene-terminated poly(2-acetoxyethyl methacrylate) macromonomer-methyl methacrylate system reported previously.

Copolymerizations of SOE macromonomer with styrene are summarized in Table 3. Copolymer composition was determined by proton NMR using the intensity ratio of the oxyethylene peak of the SOE unit to benzene-ring proton peaks of the styrene unit. Here, benzyl proton peaks due to the SOE unit are neglected because they are negligible, as can be seen in Fig. 4(A). Experimental data of the cumulative copolymer composition and

TABLE 2. Results of Free-Radical Copolymerization of SOE-II Macromonomer with Methyl Methacrylate in Benzene at 80°C[a]

Run	$f_{a,0}$, in feed[b]	Conversion x_a, %	x_b, %	x_w, %[c]	$\bar{F}_a$[d]	$\bar{F}_a$ by NMR[e]
23	0.0068	39.80	60.49	57.80	0.0045	0.0044
22		87.57	90.60	90.21	0.0066	0.0062
51	0.0098	24.64	39.93	37.25	0.0060	
55		67.47	78.92	76.91	0.0083	0.0078
62	0.0219	16.80	30.95	26.32	0.0120	0.0116
66		46.47	68.27	61.13	0.0150	
67		67.47	89.93	82.57	0.0165	0.0165
41	0.0332	15.27	28.49	22.83	0.0181	
48		21.55	48.74	37.10	0.0150	0.0152
49		44.19	72.62	60.45	0.0205	0.0202
33	0.0664	16.99	31.24	22.58	0.0372	0.0368
34		43.45	71.51	54.46	0.0414	
35		73.66	95.30	82.15	0.0521	0.0518

[a] Total concentration of monomers: 1.0 mol/L.

[b] Mole fraction of SOE in monomer feed.

[c] Total conversion as weight fraction.

[d] Mole fraction of SOE unit in the graft copolymer.

[e] Calculated from intensity ratio of oxyethylene proton peak of the SOE unit to α-methyl proton peaks of the methyl methacrylate unit.

corresponding conversion are plotted in Fig. 7. The mole fraction of SOE units in the copolymer is only slightly lower than that of SOE in the feed although these differences increase with feed composition in the experimental range used. Monomer reactivity ratios for the copolymerization of SOE with styrene were found to be $r_a = 0.86$ and $r_b = 1.20$ from the experimental data by using the integral expression for binary copolymerization [9], indicating

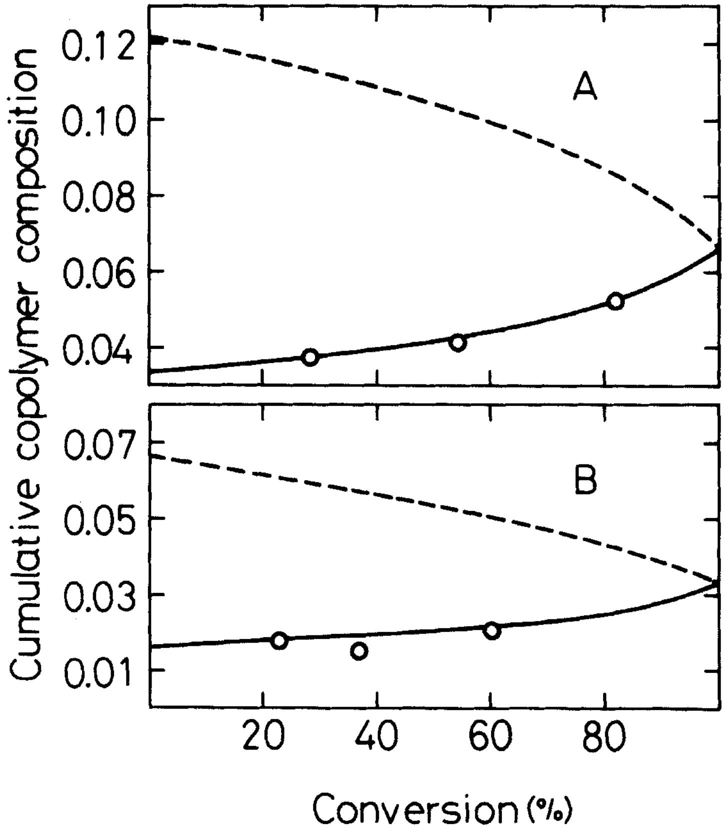

FIG. 5. Relationship between cumulative copolymer composition ($\bar{F}_a$) and conversion for the copolymerization of SOE-II macromonomer with methyl methacrylate at 80°C. Experimental data for feed SOE composition ($f_{a,0}$) of 6.64 mol% (A) and 3.32 mol% (B). Broken lines denote calculated values for styrene ($r_a = 0.52$)-methyl methacrylate ($r_b = 0.46$). Solid lines denote calculated values for $r_a = 0.06$ and $r_b = 2.0$, the values estimated for the copolymerization.

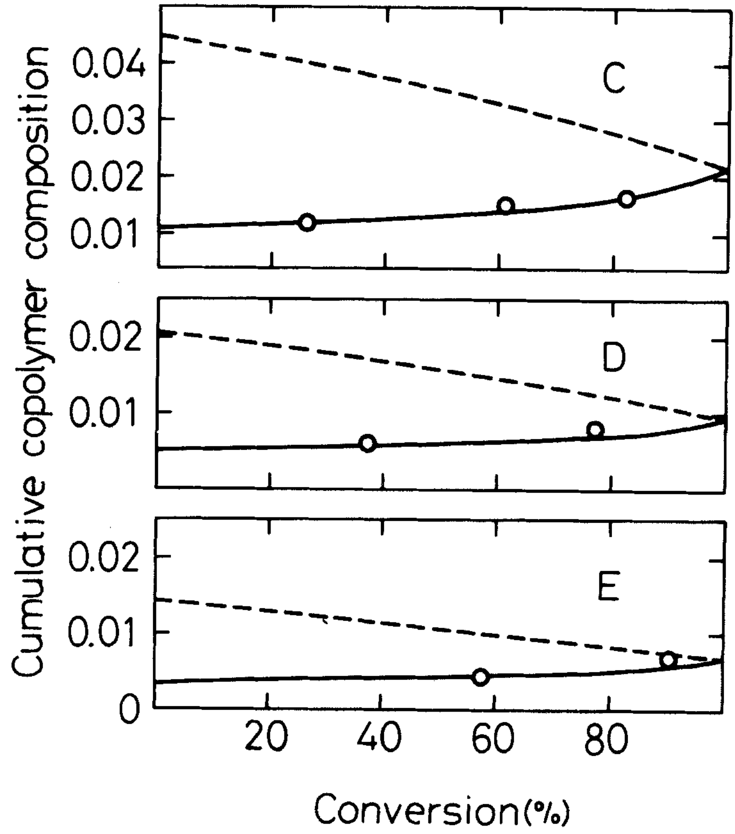

FIG. 6. Cumulative copolymer composition ($\bar{F}_a$) as a function of conversion for the copolymerization of SOE-II macromonomer with methyl methacrylate at 80°C. SOE macromonomer in feed ($f_{a,0}$): 2.19 (C), 0.98 (D), and 0.68 mol% (E). Broken lines denote calculated values for the styrene ($r_a = 0.52$)-methyl methacrylate ($r_b = 0.46$) system. Solid lines are calculated for $r_a = 0.06$ and $r_b = 2.0$, the values estimated.

TABLE 3. Results of Free Radical Copolymerization of SOE-II Macromonomer with Styrene in Benzene at 80°C[a]

Run	$f_{a,0}$, in feed[b]	Conversion X_w	$\bar{F}_a$ by NMR[c]	x_a,[d] %	x_b,[d] %
73	0.0035	33.50	0.0030	28.95	33.83
75		55.22	0.0031	49.26	55.64
74		80.67	0.0033	76.13	81.00
94	0.0146	27.04	0.0131	24.80	27.68
92		56.42	0.0131	51.33	58.00
98		81.20	0.0140	78.59	82.01
6	0.0171	12.70	0.0140	10.90	13.36
7		37.28	0.0146	32.73	38.93
4		47.94	0.0156	44.13	49.33
2		52.29	0.0153	48.13	53.80
5		58.33	0.0143	51.00	61.00
82	0.0294	22.70	0.0251	20.49	24.10
83		39.80	0.0262	36.33	42.00
86		71.22	0.0270	67.42	73.60
14	0.0422	16.57	0.0341	14.67	18.33
16		27.57	0.0386	25.67	29.33
12		52.70	0.0368	48.81	56.29
18		71.19	0.0390	68.16	74.00

[a] Total concentration of monomers: 1.0 mol/L.

[b] Mole fraction of SOE in monomer feed.

[c] Calculated from intensity ratio of oxyethylene proton peak of the SOE unit to benzene-ring proton peaks of the styrene unit.

[d] Calculated from cumulative copolymer composition ($\bar{F}_a$) and corresponding total conversion (X_w). The suffixes a and b denote SOE and styrene, respectively.

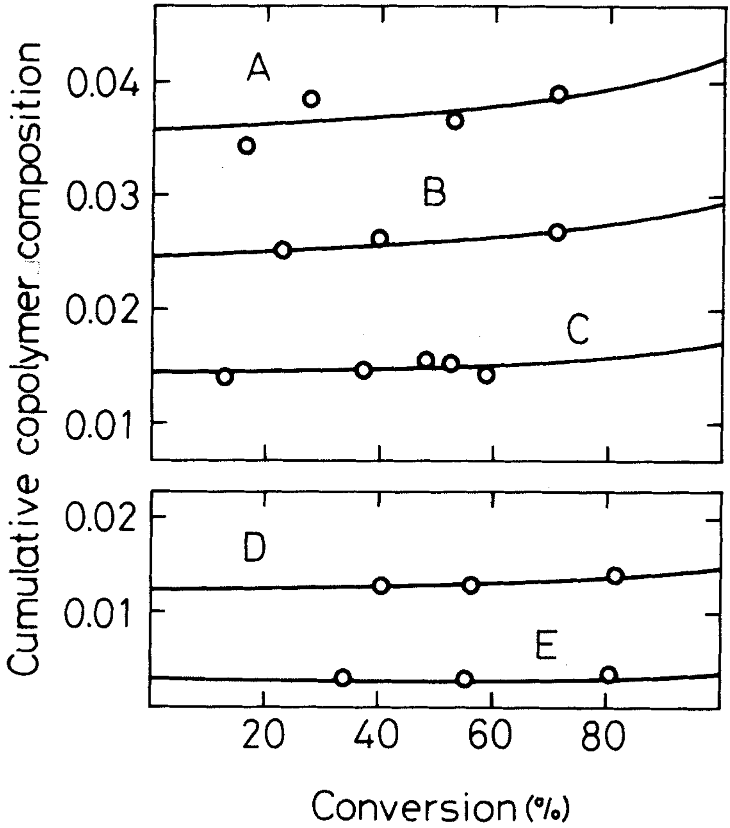

FIG. 7. Plots of experimental data of 4.22 (A), 2.94 (B), 1.71 (C), 1.46 (D), and 0.35 mol% (E) of SOE macromonomer in the feed for the copolymerization of SOE macromonomer and styrene at 80°C. Estimated values of this copolymerization system with $r_a = 0.86$ and $r_b = 1.20$ shown as solid lines.

that SOE macromonomer in this system is not significantly different from styrene.

To confirm this point, conversion of SOE (x_a) and conversion of styrene (x_b) were calculated by Eqs. (3) and (4), respectively, by use of experimental data from both cumulative copolymer composition ($\bar{F}_a$) and total conversion in weight fraction (X_w) (Table 3).

$$x_a = \frac{\dfrac{M_a}{M_b} + \dfrac{1 - f_{a,0}}{f_{a,0}}}{\dfrac{M_a}{M_b} + \dfrac{1 - \bar{F}_a}{\bar{F}_a}} X_w \tag{3}$$

$$x_b = \frac{f_{a,0}(1 - \bar{F}_a)}{\bar{F}_a(1 - f_{a,0})} x_a \tag{4}$$

Conversion of SOE and of styrene obtained above are plotted versus total conversion in Fig. 8. For all feed compositions, the experimental plots show good fits to the theoretical lines. It is clear from these data that the reactivity

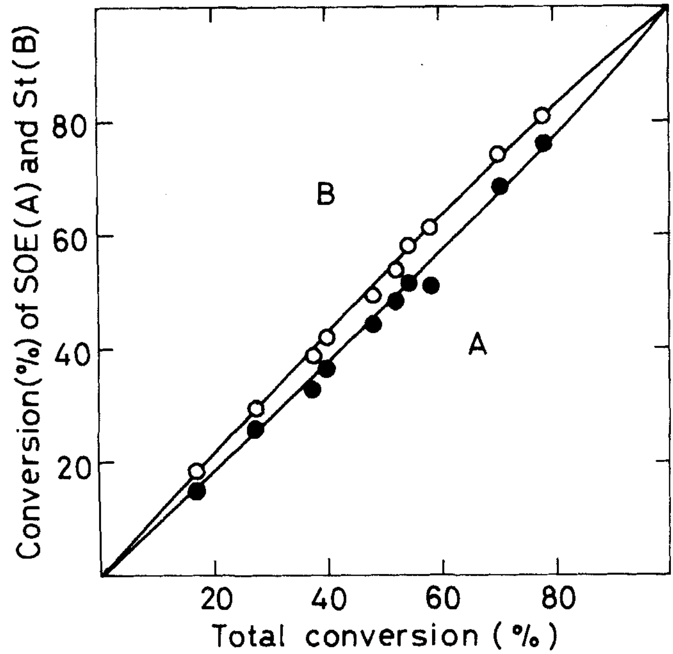

FIG. 8. Mol% conversion of SOE macromonomer (A) and of styrene (B) versus total wt% conversion for the copolymerization of SOE with styrene. Experimental data are shown as filled circles (SOE) and open circles (styrene). Solid lines denote values calculated from data of copolymer composition and total conversion, as described in Table 3.

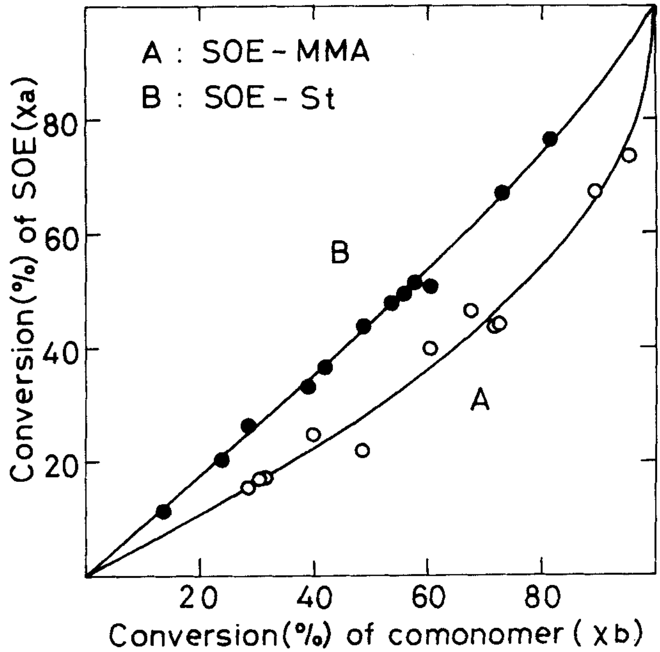

FIG. 9. Comparison of the reactivity of SOE macromonomer in the copolymerization with styrene (B) and methyl methacrylate (A). Circles denote experimental data.

of styryl double bonds in macromonomer is almost comparable to styrene, although close inspection of the data in Fig. 8 shows that x_a is somewhat less than x_b.

To compare the reactivity of SOE, the relationship between conversion of SOE and of styrene or methyl methacrylate are shown in Fig. 9. For SOE and styrene, the relationship between conversion of SOE and conversion of comonomer lies near a diagonal line, i.e., this system exhibits nearly ideal behavior. For methyl methacrylate, conversion of SOE lies below the diagonal.

Figure 10 compares feed monomer composition and instantaneous copolymer composition curves for SOE-styrene and SOE-methyl methacrylate copolymerization. Instantaneous copolymer compositions were calculated from the estimated values in all but the styrene-methyl methacrylate system. It is clear that the reactivity of SOE macromonomer is markedly different

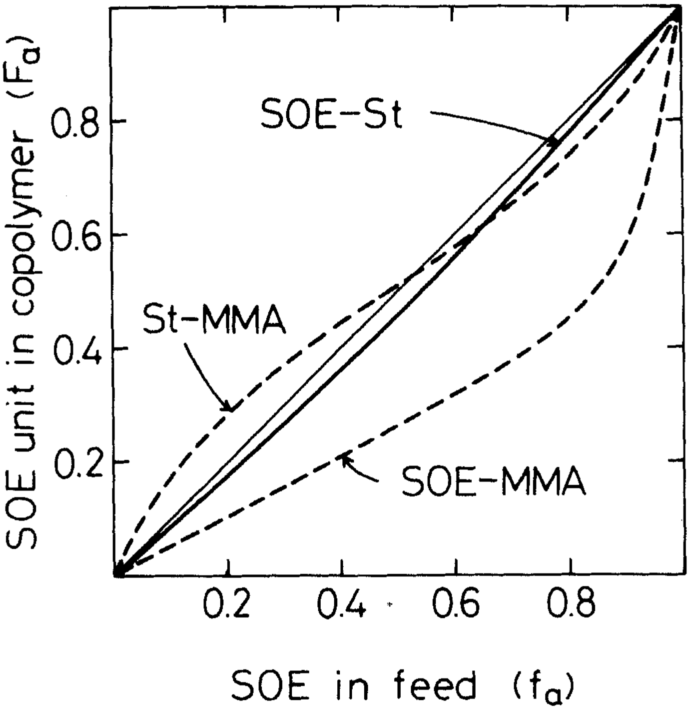

FIG. 10. Feed monomer composition and instantaneous copolymer composition curves calculated from experimental copolymerization parameters for the copolymerization of SOE with styrene and methyl methacrylate.

in the two copolymerization systems. Although the effect is not yet understood, it is probably connected to the affinity for comonomer and the hydrophobicity of SOE.

As shown in Table 4, the number-average molecular weight of the graft copolymer increases with decreasing mole fraction of SOE units in the copolymer for both type of graft copolymers. Number-average degrees of polymerization of the graft copolymers obtained are tenfold those of the SOE homopolymers. The number of graft chains on each graft copolymer molecule, $\bar{N}_g$ are calculated by

$$\bar{N}_g = \frac{\bar{F}_a M_n}{\bar{F}_a M_a + (1 - \bar{F}_a) M_b}, \tag{5}$$

TABLE 4. Number-Average Molecular Weights of Typical Samples of the Copolymer of SOE with Styrene and with Methyl Methacrylate

Run	Copolymer of SOE with	$f_{a,0}$[a]	$\bar{F}_a$[b]	Conversion,[c] %	$\bar{M}_n \times 10^{-3}$	$\bar{N}_g$[d]
66	MMA	0.0219	0.0150	61.13	79.46	9.08
34	MMA	0.0664	0.0414	54.46	54.85	12.20
92	Styrene	0.0146	0.0131	56.42	73.75	7.36
16	Styrene	0.0422	0.0386	27.57	8.78	

[a] Mole fraction of SOE in feed.

[b] Mole fraction of SOE units in copolymer.

[c] Total weight conversion.

[d] Number of poly(oxyethylene) graft chains (macromonomer) on each copolymer molecule, calculated by Eq. (5).

where $\bar{M}_n$ is the number-average molecular weight of graft copolumer. The values of $\bar{N}_g$ increase slightly with increasing mole fraction of SOE unit in the copolymer (Table 4) in spite of decreasing molecular weight of graft copolymer in both copolymerization systems.

Catalytic Activities of the Graft Copolymers

We checked the performance of the copolymer containing poly(oxyethylene) graft chains as an activator of the organic reaction. For this purpose we used the halogen exchange reaction, as shown in Scheme 1.

The plots of 1-bromooctane remaining as a function of time in the presence and the absence of the graft copolymer (Fig. 11) gave straight lines up to conversions of at least 25%, and the slopes in this range were used to calculate pseudo-first-order rate constants (k). Activities of the copolymers of SOE were evaluated by use of the observed rate constants. For the parent poly(oxyethyl-

$$C_8H_{17}Br + NaI \xrightarrow[80^\circ C \text{ in toluene}]{\text{graft copolymer}} C_8H_{17}I + NaBr$$

SCHEME 1.

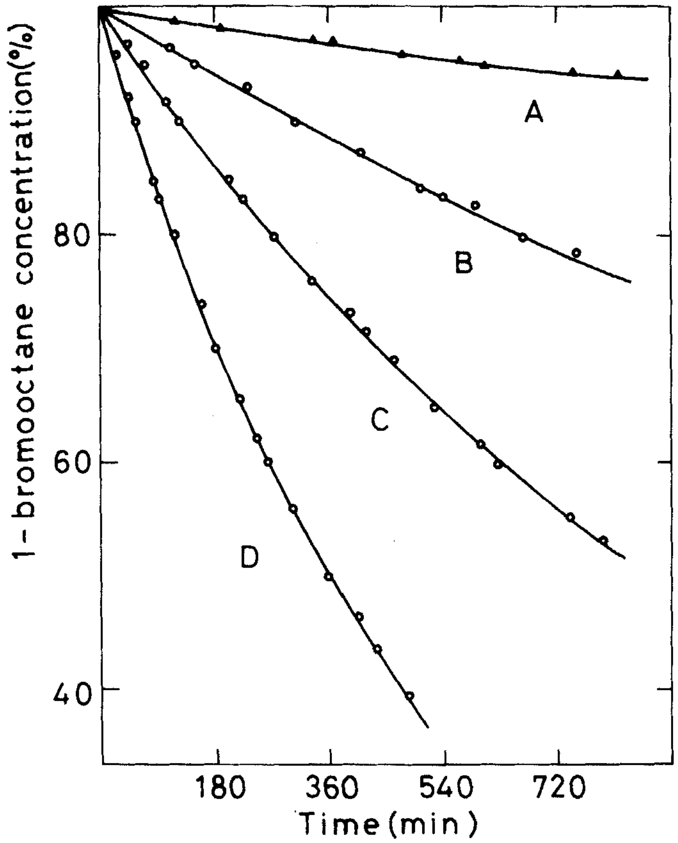

FIG. 11. Relationship between percent of 1-bromooctane remaining and time for the reaction of 1-bromooctane with sodium iodide in the absence (A) and presence (B-D) of the graft copolymer of SOE and methyl methacrylate (Run 66) in toluene at 80°C. Concentration of oxyethylene unit of SOE: 15.0 (B), 39.9 (C), and 78.0 mmol/L (D).

ene), the rate constant was in agreement within experimental error with that in the absence of the graft copolymer, independent of the oxyethylene unit concentrations in the range 15.0 to 40.0 mmol/L.

To elucidate the relation of the catalytic activities and the chemical structure, the concentration of oxyethylene units was kept constant and the copolymer composition of SOE was varied (Table 5). When the oxyethylene

TABLE 5. Dependence of Pseudo-First-Order Rate Constant (k) on Composition of the SOE Copolymers in the Reaction[a]

Run	Copolymer of SOE with	$\bar{F}_a$[b]	$k \times 10^5$ s^{-1}	
			15.0[c]	40.0[c]
22	MMA	0.0066	1.36	3.76
55	MMA	0.0083	0.78	2.56
66	MMA	0.0150	0.61	1.56
33	MMA	0.0372	0.32	0.88
74	Styrene	0.0033	2.40	6.56
92	Styrene	0.0131	1.08	3.12

[a] Reaction of 1-bromooctane with 5 mol equivalent sodium iodide carried out in toluene at 80°C.

[b] Mole fraction of SOE unit in copolymer.

[c] Constant concentration of oxyethylene unit of SOE in the copolymers (in mmol/L).

concentration was kept constant at 15.0 and 40.0 mmol/L, the rate constant increased with decreasing mole fraction of SOE unit in the copolymer of SOE and methyl methacrylate over the whole range from 0.0066 to 0.0372. A similar tendency was observed for the copolymers of SOE and styrene. From these data it appears that the activity of the SOE copolymer catalysts derived from copolymerization with styrene is higher than that of the corresponding methyl methacrylate copolymer catalyst. More detailed results for the reaction with these copolymers as activators will be described in a future publication.

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Received March 12, 1987
Revision received April 20, 1987