SYNTHESIS OF ABA TYPE TRIBLOCK COPOLYMERS BY RADICAL POLYMERIZATION WITH 1,4-BIS(*p*-TERTBUTYLPHENYLSELENOMETHYL) BENZENE AS A PHOTOINIFERTER

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ABSTRACT

1,4-Bis(*p-tert*-butylphenylselenomethyl)benzene was used as a bifunctional photoiniferter for the polymerization of methyl methacrylate (MMA). Both the polymer yields and the number average of molecular weights ($\overline{M}_n$) of polymers increased with the polymerization time and the $\overline{M}_n$ linearly increased with polymer yield. The addition of MMA to the poly(MMA) with irradiation increased the $\overline{M}_n$ of the polymer. Photoirradiation of telechelic polystyrene having phenylseleno groups at both ends as polymeric photoiniferter in the presence of MMA or *p*-chloromethylstyrene afforded effectively corresponding to the ABA type triblock copolymers. On the other hand, photopolymerization of *p*-methylstyrene with ABA type triblock copolymer of styrene and *p*-chloromethylstyrene as polymeric photoiniferter afforded to multiblock copolymer of styrene and *p*-substituted styrenes.

Key Words: 1,4-Bis(*p-tert*-butylphenylselenomethyl) benzene; Radical polymerization; Photoiniferter; Polymeric photoiniferter; Methyl methacrylate; *p*-Chloromethylstyrene; *p*-Methylstyrene; Triblock copolymers; Multiblock copolymers.
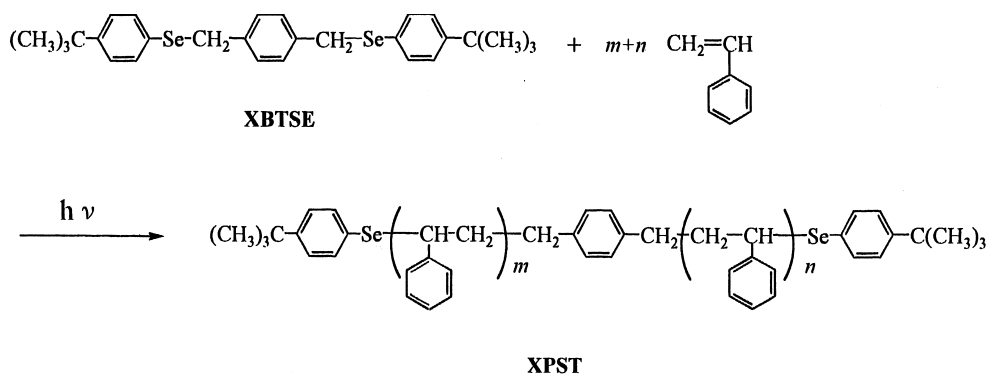
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INTRODUCTION

Well-defined triblock copolymers of ABA type represent an interesting field of research due to their industrial applications, such as preparation of thermoplastic elastomers [1]. Generally speaking, ABA type triblock copolymers are obtained by several methods, such as sequential monomer addition using living polymerization, linking reaction of diblock copolymers, and the use of telechelic polymer as bifunctional initiator [2–6]. Among them, telechelic polymer method, which prepared by radical polymerization with bifunctional iniferter, is attractive for preparing simple ABA type triblock copolymers and more complex polymer architectures using various monomers which can not polymerize by another mechanism. In fact, Otsu *et al.* [7, 8] reported the synthesis of ABA type triblock copolymers with telechelic polymer, which was prepared from xylylene bis(N,N-diethyldithiocarbamate) as an effective bifunctional photoiniferter. In previous papers [9, 10], we reported a synthesis of well-defined AB type (**BPST-b-PMMA**, etc.) and ABC type (**BPST-b-PMS-b-PBS**) block copolymers by monofunctional polystyrene (**BPST**), prepared with benzyl phenyl selenide (**BPSE**) as a photoiniferter, as polymeric photoiniferter (Scheme 1). Most recently, we also carried out the synthesis of block copolymer by bifunctional polystyrene, which prepared with diphenyl diselenide as a photoiniferter [11]. However, the formation of resulting block copolymer was not clear. It indicated that diphenyl diselenide, such as unsymmetrical photoiniferter, is poor efficiently worked for synthesis of ABA type triblock copolymer. Therefore, we

$R_1 = H, R_2 = C_6H_5Br, C_6H_5CH_3, C_6H_5CH_2Cl, C_6H_5CH_2OCOCH_3$

or

$R_1 = CH_3, R_2 = COOCH_3$

BPST-b-PBS, PMS, PCMS, PVBAc

or

BPST-b-PMMA

BPST-b-PMS-b-PBS
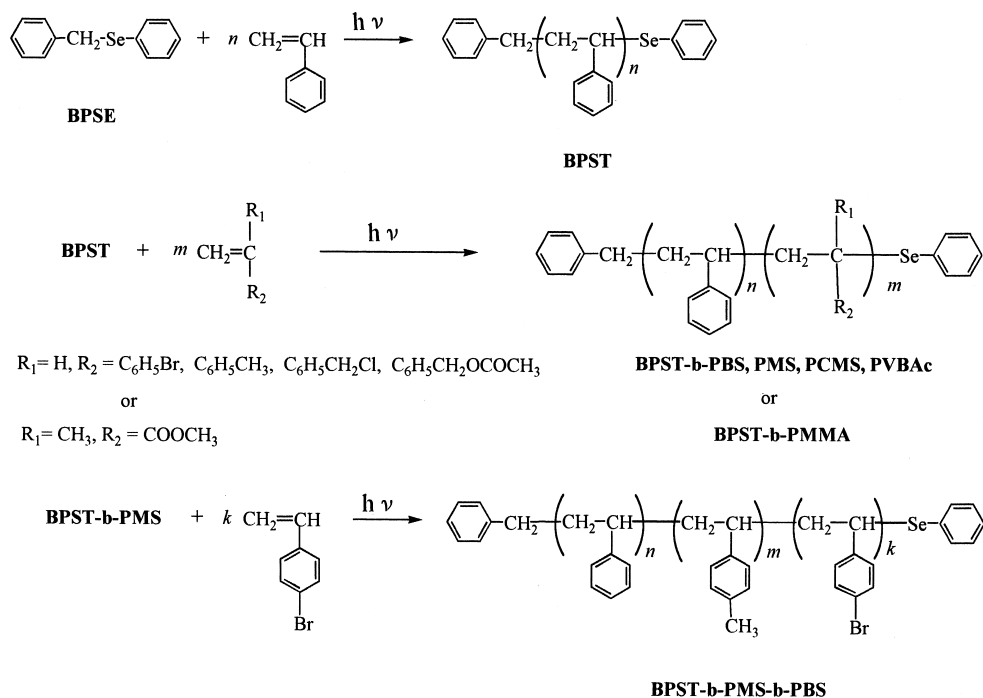
Scheme 1.

Scheme 2.

expected that a symmetrical photoiniferter, such as 1,4-bis(*p-tert*-butylphenylse-lenomethyl) benzene (**XBTSE**), could result in the synthesis of a well-defined ABA type triblock copolymer. **XBTSE**, which consists of a identical bond as **BPSE**, worked as a photoiniferter in polymerization of styrene previously described [12]. The resulting polymer was a well-defined telechelic polystyrene (**XPST**) having arylseleno groups at both chain ends (Scheme 2). This paper describes the synthesis of well-defined ABA type triblock copolymers by radical photopolymerization of MMA or *p*-chloromethylstyrene (CMS) with **XPST**. The synthesis of multiblock copolymer of *p*-methylstyrene (MS) with ABA type triblock copolymer of styrene and CMS as polymeric photoiniferter is also investigated.

EXPERIMENTAL

Materials

Styrene, MMA, CMS, and MS were purified by the ordinary method and distilled in a stream of nitrogen just before use. **XBTSE** was prepared as in a previous paper [12]. Solvents were purified by distillation after appropriate drying. Other reagents were obtained commercially and used without further purification.

Photopolymerization of MMA with XBTSE

XBTSE (24.7 mg, 0.047 mmol) and MMA (5 mL) ([**XBTSE**]/[MMA] = 0.001) charged into a Pyrex tube. The tube was degassed under vacuum by the conventional freeze and thaw technique, and sealed off under vacuum. All polymerizations were carried out by irradiation with a Riko 100 W high-pressure mercury lamp from a 8 cm distance at room temperature. After a given time, the tube was opened, and its content was poured into a large amount of n-hexane. The resulting polymer was then purified by reprecipitation from methylene chloride with n-hexane, followed by drying in vacuum. The yield of polymers was determined from the weight of the dried polymers obtained.

Photopolymerization of MMA with XPMMA1 as a Polymeric Photoiniferter

A sample of **XPMMA1** (0.2 g), MMA (3 mL) and benzene (2 mL) was charged into a Pyrex tube. These solutions were irradiated with a high-pressure mercury lamp from a 8 cm distance for 2 hours at room temperature. The reaction mixture was poured into n-hexane, and the resulting polymer (**XPMMA2**) was dried in vacuum. The yield of polymers was determined from the weight of the dried polymers obtained.

Synthesis of Polystyrenes (XPST1 and XPST2) as a Polymeric Photoiniferter

A solution of **XBTSE** (0.28 g, 0.53 mmol) and styrene (6 mL) ([**XBTSE**]/ [styrene] = 0.01) was immersed in a Pyrex tube. The tube was degassed under vacuum by conventional freeze and thaw techniques, and sealed under vacuum. The solution was irradiated with the 100 W high pressure mercury lamp for 10 hours. The tube was opened and the contents were poured into methanol. The resulting polystyrene, **XPST1**, was reprecipitated from methylene chloride to methanol. (Yield, 2.30 g, 42.3%). On the other hand, **XPST2** was obtained from irradiation to a solution of **XBTSE** (0.58 g, 1.10 mmol), styrene (5 mL) ([**XBTSE**]/[styrene] = 0.025), and benzene (2 mL) for 24 hours, it was treated by the same method above. (Yield, 1.03 g, 22.8%).

Synthesis of ABA Type Triblock Copolymer of Styrene and Methyl Methacrylate (XPMMA-b-PST-b-PMMA)

A solution of **XPST1** (0.2 g), MMA (3 mL) ([**XPST1**]/[MMA] = 0.0021) and benzene (2 mL) in a Pyrex tube was irradiated with a 100 W high pressure mercury lamp from a 8 cm distance at room temperature for 8 hours. The resulting polymer (**P-1**) was poured into methanol. The yield was 0.92 g. Polystyrene was extracted from the **P-1** (0.2 g) with of cyclohexane (100 ml) by a soxhlet extractor. The resulting polystyrene was reprecipitated from methylene chloride to n-hexane in order to confirm the presence of constituent of poly(MMA). Then, poly(MMA) was extracted with a mixture of benzene and methanol (10 mL: 28 mL). The residue was dissolved with methylene chloride and poured into methanol. The resulting block copolymer, **XPMMA-b-PST-b-PMMA**, was dried in vacuum. The polymer fractions thus extracted were also examined by GPC and ^{1}H- NMR analysis.

Synthesis of ABA Type Triblock (XPCMS-b-PST-b-PCMS) and Multiblock Copolymers of Styrene and *p*-Substitude Styrene (XPMS-b-PCMS-b-PST-b-PCMS-b-PMS)

A solution of **XPST2** (0.3 g, 0.14 mmol), CMS (1.04 g) ([**XPST2**]/[CMS] = 0.02) and benzene (1 mL) in Pyrex tube was irradiated with a 100 W high pressure

mercury lamp from a 8 cm distance for 25 hours at room temperature. The resulting polymer was poured into methanol. The yield was 0.54 g. The composition of **XPCMS-b-PST-b-PCMS** were examined by GPC and ^{1}H NMR analysis. On the other hand, a solution of MS (0.62 g) and **XPCMS-b-PST-b-PCMS** (0.1 g, 0.03 mmol) ([**XPCMS-b-PST-b-PCMS**]/[MS] = 0.005) in a Pyrex tube was irradiated with the high-pressure mercury lamp at room temperature for 24 hours. The polymer mixture was poured into methanol. The yield was 0.23 g. The composition of **XPMS-b-PCMS-b-PST-b-PCMS-b-PMS** were examined by GPC and ^{1}H NMR analysis.

Measurements

^{1}H-NMR spectra were recorded by JEOL JNM-GX400 (400MHZ) or BRUKER AVANCE200 FT-NMR (200 MHZ) spectrometers with CDCl$_3$ as solvent using tetramethylsilane as the internal standard. Gel permeation chromatography (GPC) was performed on a TOSOH HLC-803D with G2000, G3000, and GMH TSK gel-columns and a differential refractometric detector using THF as an eluent. The molecular weights were determined using polystyrene standards. IR spectra were measured by a Nicolet Impact-400D.

RESULTS AND DISCUSSION

Photopolymerization of MMA in the Presence of XBTSE

To investigate the behavior of **XBTSE** in photopolymerization of MMA, the polymerization was carried out on irradiation to a solution of MMA and **XBTSE** (0.001 molar equiv. relative to monomer) in a Pyrex tube at room temperature. Figure 1 shows the time-yield and time-average number molecular weight ($\overline{M}_n$) relations in the photopolymerization of MMA with **XBTSE**. Both values of polymer yield and $\overline{M}_n$ of the resulting polymers are increased with reaction time. Moreover, $\overline{M}_n$ increased linearly with polymer yield as shown in Figure 2. These results indicate that **XBPSE** worked as an effective photoiniferter in radical polymerization of MMA. However, the $\overline{M}_n$ – yield lines did not intersect the origin of the graph. It seems that slight photopolymerization, regardless of iniferter due to very fast rate of MMA, cannot be negligible in the early step of the polymerization [9, 11].

Photopolymerization of MMA with **PMMA1** as a starting polymer was carried out for 2 hours in order to confirm the reactive chain ends of resulting poly(MMA). As shown in Figure 3, the peak in GPC for **PMMA2** shifted to the higher molecular weight region in comparison with the starting polymer, **PMMA1**. Furthermore, from the weight of the resulting polymer and $\overline{M}_n$, it was found that the number of polymer molecules through the polymerization reaction almost unchanged (2.0–2.4×10^{19}). This result shows that the resulting poly(MMA) has active chain ends with phenylseleno groups, and it effectively worked as a poly-
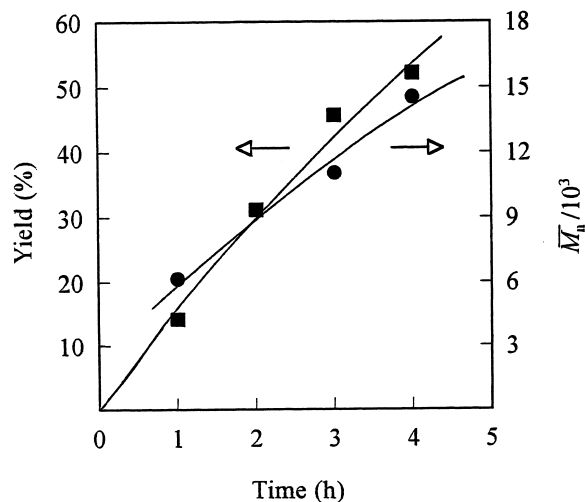
Figure 1. Time-yield (■) and time-$\overline{M}_n$ (●) relations in photopolymerization of MMA with **XBTSE** as a photoiniferter. [MMA] = 9.4 mol/L, [**XBTSE**]/[MMA] = 0.001.

Figure 2. Yield - $\overline{M}_n$ (■) and yield - $\overline{M}_w/\overline{M}_n$ (●) relations in photopolymerization of MMA with **XBTSE** as a photoiniferter. [MMA] = 9.4 mol/L, [**XBTSE**]/[MMA] = 0.001.
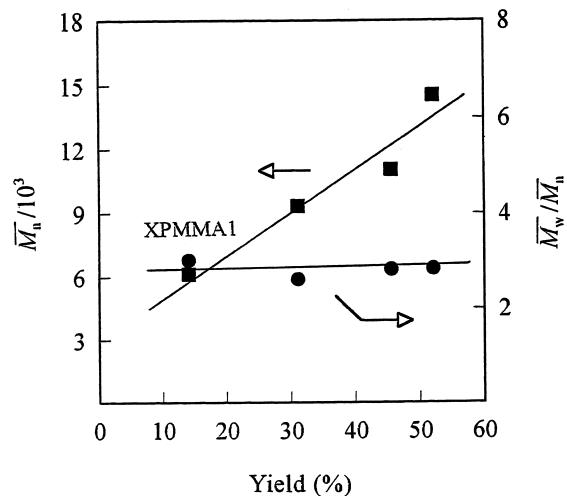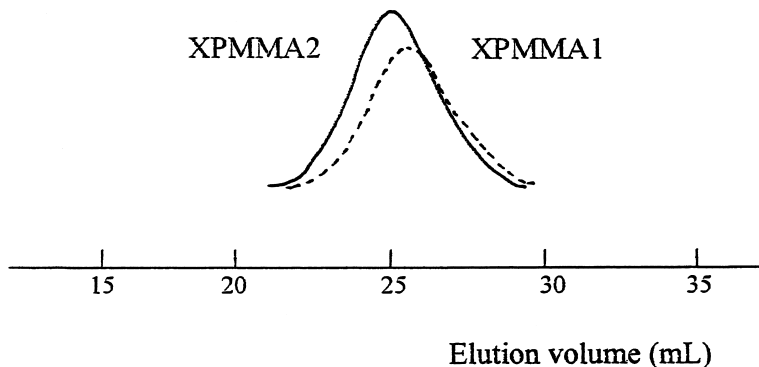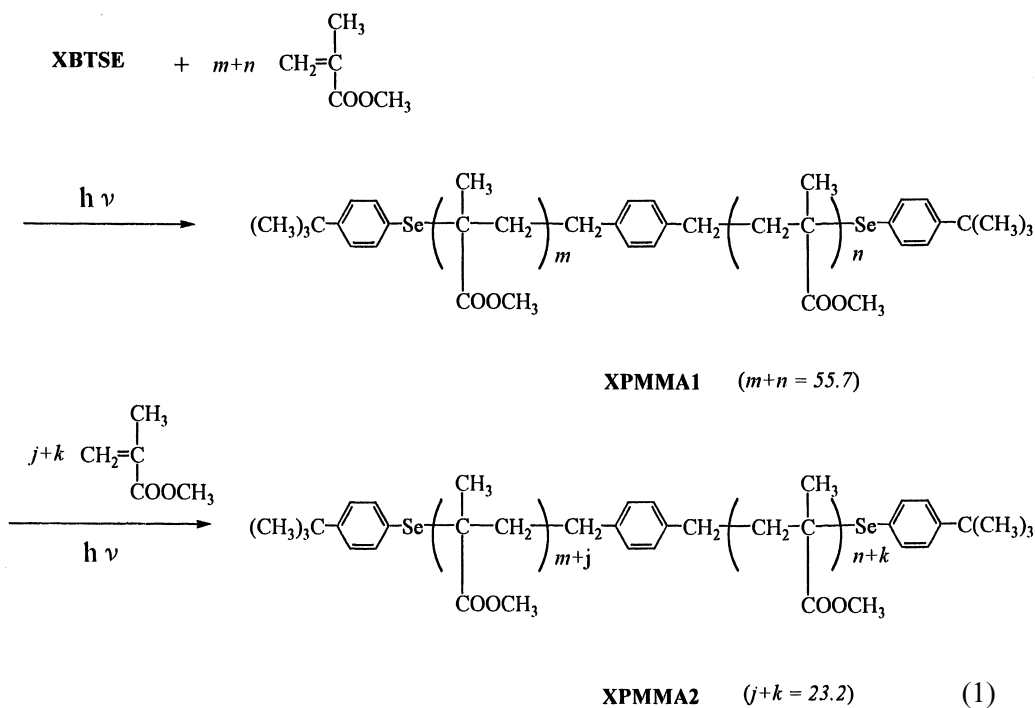

Figure 3. GPC profiles of **XPMMA2** (solid line, $\overline{M}_n = 8,400$, $\overline{M}_w/\overline{M}_n = 2.20$) and XPMMA1 (broken line, $\overline{M}_n = 6,100$, $\overline{M}_w/\overline{M}_n = 3.03$).

$$\text{XBTSE} \quad + \quad m+n \quad CH_2=\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}$$

$$\xrightarrow{\quad h\nu \quad}$$

$$(CH_3)_3C-\langle\rangle-Se\left(\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2\right)_m CH_2-\langle\rangle-CH_2\left(CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\right)_n Se-\langle\rangle-C(CH_3)_3$$

XPMMA1   (*m+n = 55.7*)

$$j+k \quad CH_2=\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}$$

$$\xrightarrow{\underset{h\nu}{\quad\quad}}$$

$$(CH_3)_3C-\langle\rangle-Se\left(\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2\right)_{m+j} CH_2-\langle\rangle-CH_2\left(CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\right)_{n+k} Se-\langle\rangle-C(CH_3)_3$$

XPMMA2   (*j+k = 23.2*)   (1)

meric photoiniferter. From the above results, photopolymerization of MMA with **XBPSE** was shown to proceed as in Equation 1. Therefore, **XBTSE**, which consists of a identical bond as **BPSE**, worked as a photoiniferter in polymerization of MMA, and the polymerization proceeds as in essentially the same mechanisms according to the previous report for **BPSE** as a photoiniferter [9].
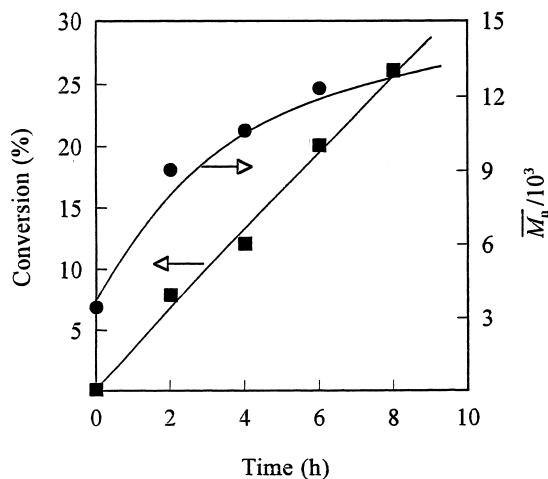

Figure 4.   Time-conversion (■) and time-$\overline{M}_n$ (●) relations in photopolymerization of MMA with **XPST1** as a polymeric photoiniferter. [MMA] = 5.6 mol/L, [**XPST1**]/[MMA] = 0.0021.
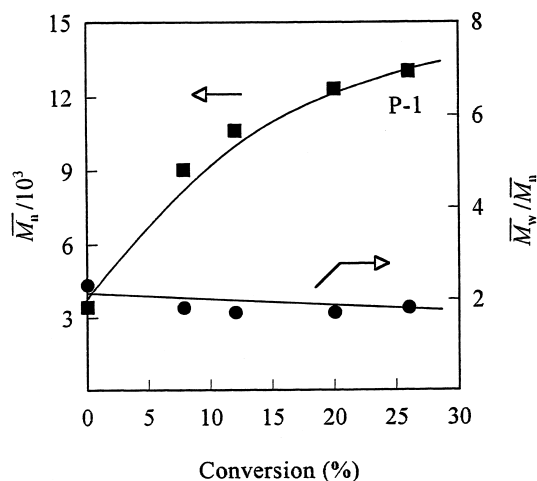
Figure 5. Conversion - $\overline{M}_n$ (■) and Conversion - $\overline{M}_w/\overline{M}_n$ (•) relations in photopolymerization MMA with XPST1 as a polymeric photoiniferter. [MMA] = 5.6 mol/L, [XPST1]/[MMA] = 0.0021.

Synthesis of ABA Type Triblock Copolymer of Styrene and MMA

To prepare the well-defined ABA type triblock copolymers, the high degree of end group functionality and small molecular weight were a prerequisite for the choice of effective polymeric photoiniferter. As noted above, the control of photopolymerization of MMA was not easy due to very fast rate of MMA in the early step of the polymerization, while determination of the end structure of telechelic poly(MMA), having high molecular weight by ^{1}H NMR analysis, was very difficult due to the very low concentration of the end groups. Therefore, the telechelic polystyrene, having phenylseleno group at chain ends, was employed as polymeric photoiniferter. First, photopolymerizations of MMA, in the presence of **XPST1** ($\overline{M}_n = 3,400, \overline{M}_w/\overline{M}_n = 2.28$, DF = 1.8), were investigated. Here, DF (degree of end group functionality) is by done comparing the $\overline{M}_n$ by GPC with the peak intensity
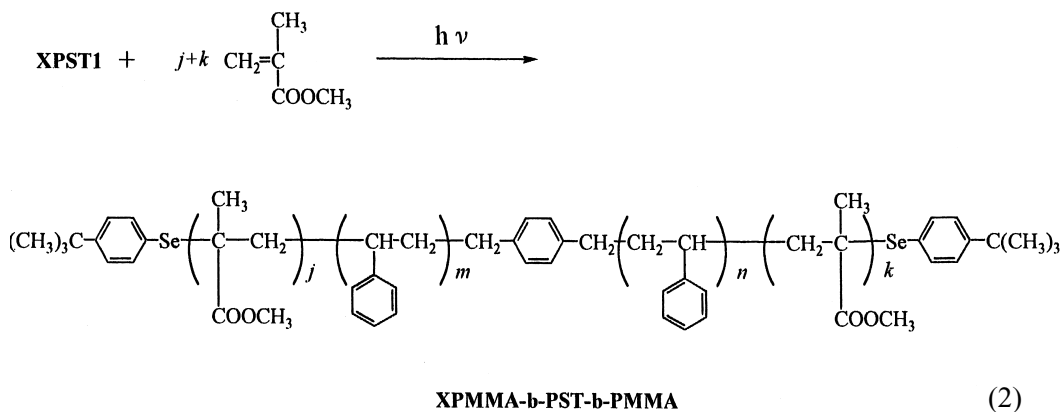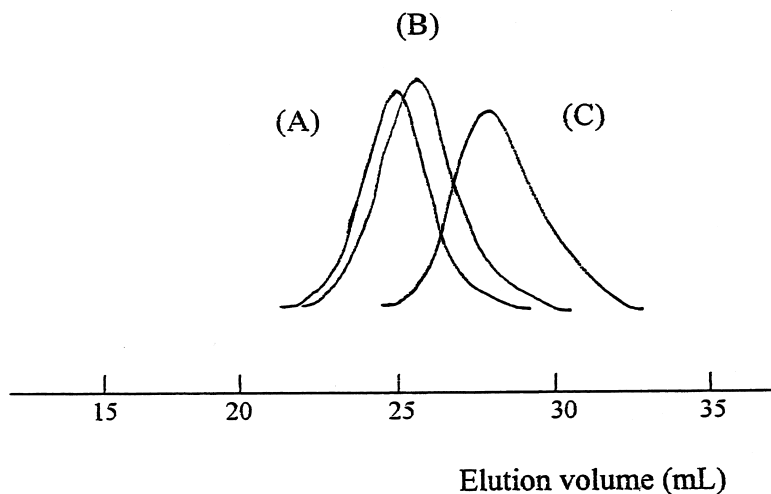

XPMMA-b-PST-b-PMMA   (2)

Figure 6. GPC profiles of (A) **XPMMA-b-PST-b-PMMA** ($\overline{M}_n$ = 17,100, $\overline{M}_w$ /$\overline{M}_n$ = 1.49), (B) original product (P-1) without solvent fractionation ($\overline{M}_n$ = 13,000, $\overline{M}_w$ /$\overline{M}_n$ = 1.78), and (C) **XPST1** as a prepolymer ($\overline{M}_n$ = 3,400, $\overline{M}_w$ /$\overline{M}_n$ = 2.28).

ratio of *tert*-butyl signal at 1.27 ppm to phenyl group signals at 6.3–7.4 ppm or to the methine signal of polystyrene backbone at 1.6–2.3 ppm in typical ^{1}H NMR spectrum of polystyrene [12]. The polymerization was carried out by irradiation of the solution of **XPST1** and MMA in benzene at room temperature. Figure 4 shows time-conversion and time-$\overline{M}_n$ relations. Both values of conversion and $\overline{M}_n$ of the resulting polymers are increased with reaction time. Moreover, $\overline{M}_n$ also increased with the conversion as shown in Figure 5. These results indicate that the polymerization proceeded smoothly by the insertion of a MMA monomer to between the end of polystyrene and phenylseleno groups as shown in Equation 2.

Among the produced polymer, **P-1** ($\overline{M}_n$ = 13,000, $\overline{M}_w$ /$\overline{M}_n$ = 1.78) was separated by a soxhlet extraction technique to give a block copolymer. The results are shown in Table 1. The yield of the isolated **XPMMA-b-PST-b-PMMA** was 70.1 wt%, and those of styrene homopolymer and MMA homopolymer were 8.5 wt% and 21.4 wt%, respectively. Here, MMA homopolymer is thought to be produced mainly by photoirradiation regardless of the polymeric photoiniferter. In the IR spectrum of the **XPMMA-b-PST-b-PMMA**, the strong band of carbonyl group at 1720 cm^{-1} attributed to PMMA segment and band of aromatic vibration at 1580 cm^{-1} attributed to PST segment were observed. Figure 6 shows GPC curves for block copolymer (**XPMMA-b-PST-b-PMMA**, (A)) after separation by appropriate solvents, the original product (**P-1**, (B)), and polystyrene prepolymer as polymeric photoiniferter (**XPST1**, (C)). The curve of (A) shows a unimodal peak, and the $\overline{M}_n$ of (A) reveals the 13,200 g/mol increased to compare that of the polystyrene prepolymer (C). On the other hand, the approximate composition of the block copolymer was determined from ^{1}H NMR in Figure 7 (A). By comparing
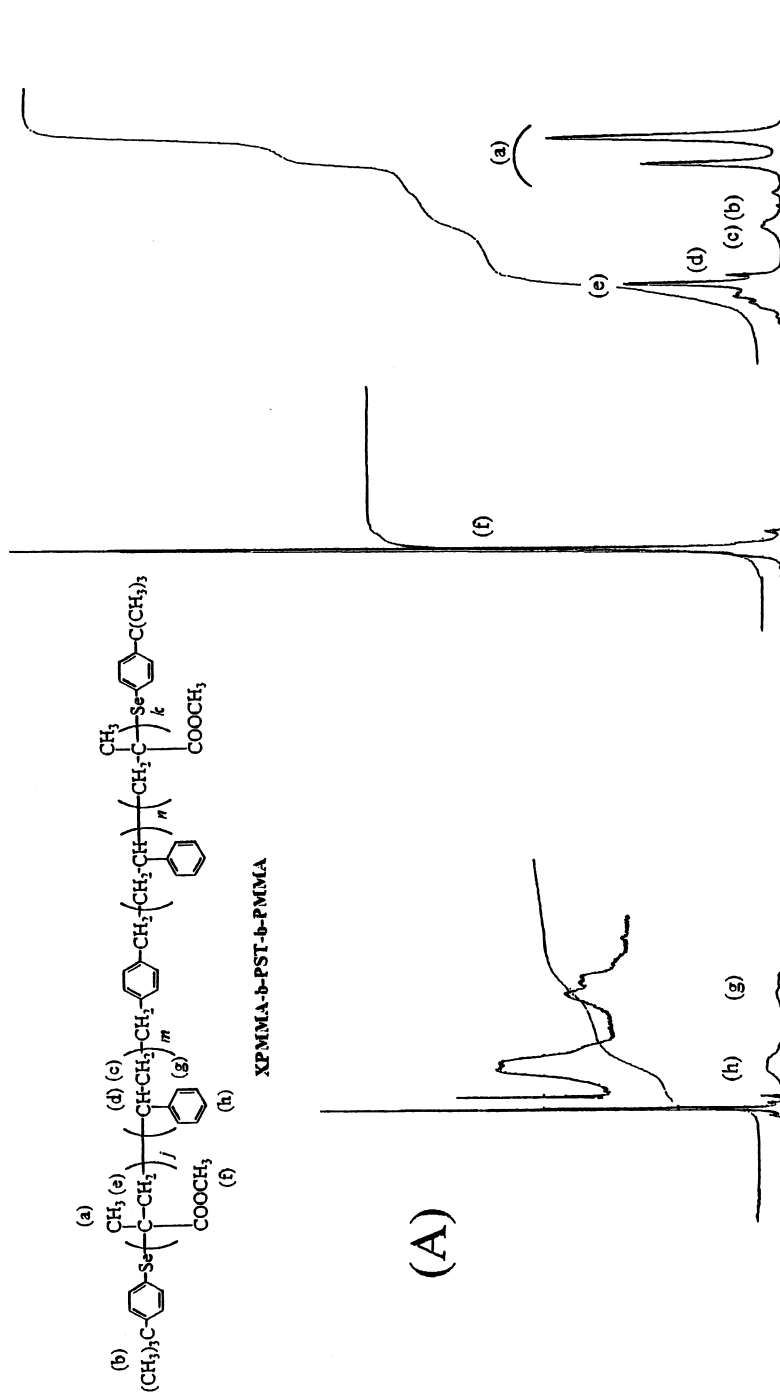
Figure 7. ^{1}H NMR spectrum (400MHz, in CDCl$_3$) of (A) **XPMMA-b-PST-b-PMMA** ($\bar{M}_n = 17{,}100$, $\bar{M}_w/\bar{M}_n = 1.49$), (B) Homo polystyrene ($\bar{M}_n = 4{,}600$, $\bar{M}_w/\bar{M}_n = 1.75$), and (C) Homo poly(MMA) ($\bar{M}_n = 7{,}900$, $\bar{M}_w/\bar{M}_n = 1.64$).
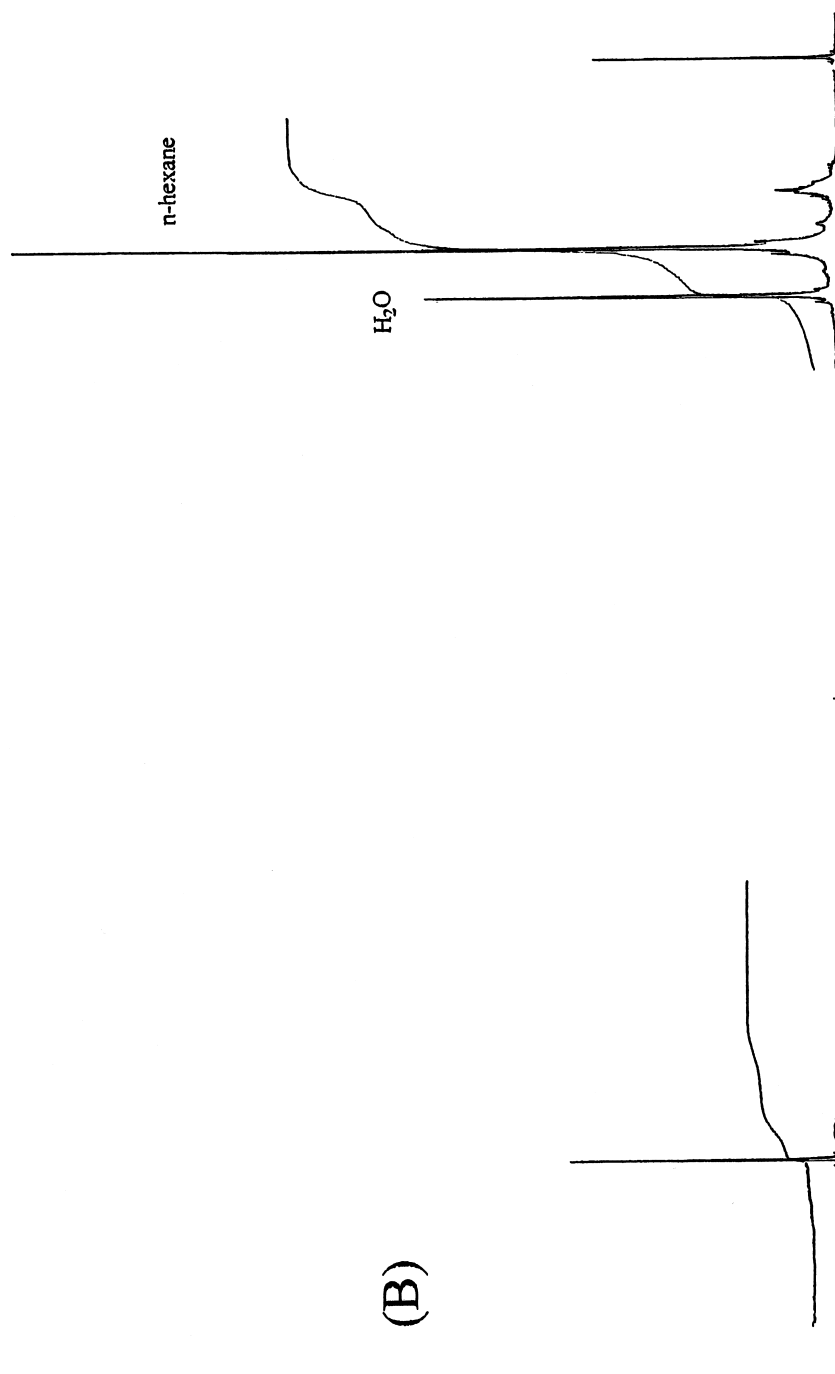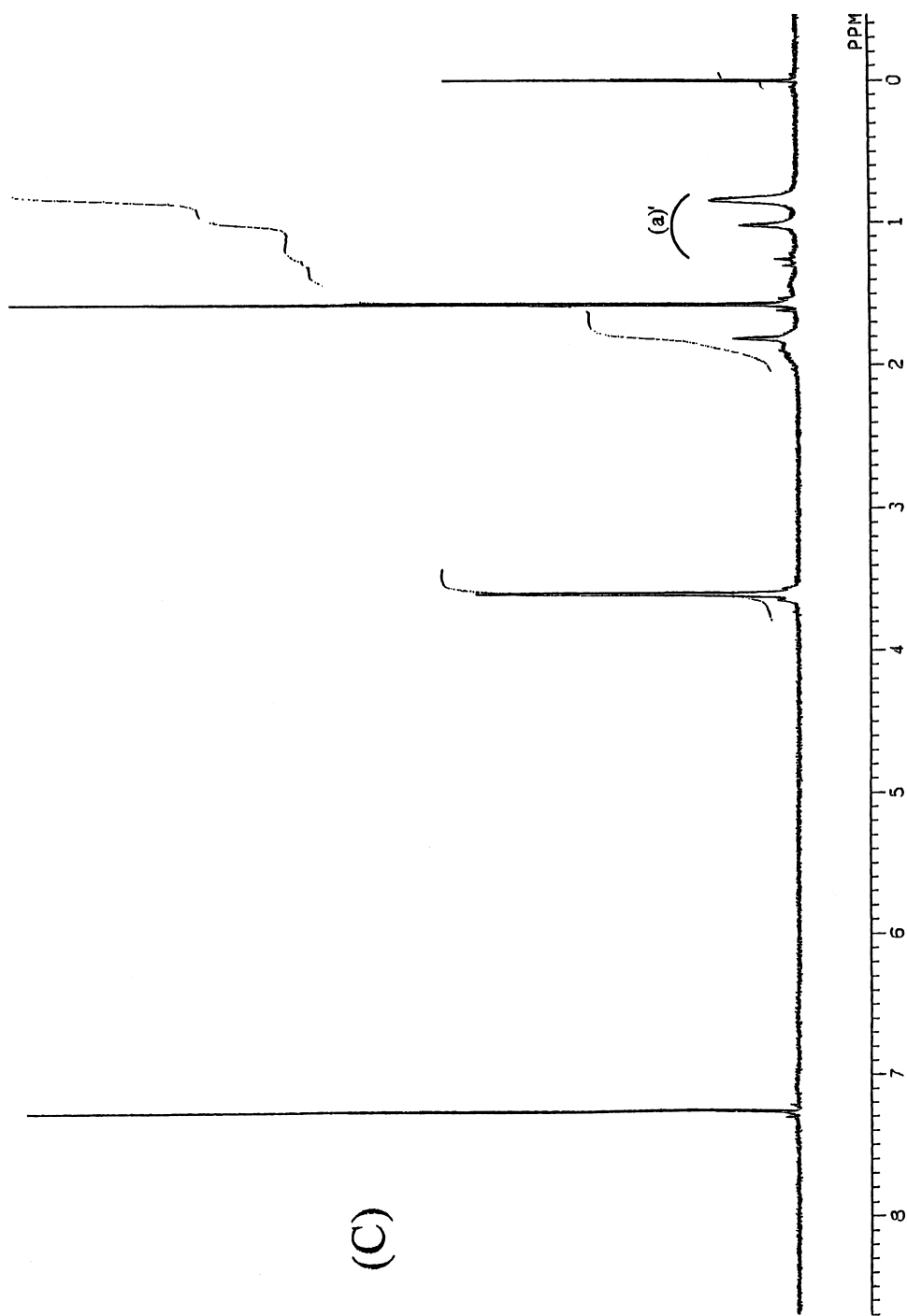
n-hexane

H₂O

(B)

Figure 7. Continued

Figure 7. Continued

Table 1. Preparation of ABA Type Triblock Copolymer of Styrene and Methyl Methacrylate (**XPMMA-b-PST-b-PMMA**)[a]

Polymer	Prepolymer			Time (h)	Total yield[c] (g)	Conversion[d] of MMA (%)	Original Product[e]			Block Copolymerization[f]		
	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	DF[b]				Polymer	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	Homo Polystyrene (g / wt%)	Homo Poly(MMA) (g / wt%)	Block Copolymer (g / wt%)
XPST1	3,400	2.28	1.8	8	0.92	25.6	**P-1**	13,000	1.78	0.08/8.5	0.20/21.4	0.64/70.1

[a]Conditions : 3 mL of MMA, 0.2 g of prepolymer (**XPST1**), and 2 mL of benzene were irradiated for 8h.
[b]DF was obtained from GPC and ^{1}H NMR analysis.
[c]Weight of polymer precipitated with methanol (gross polymer).
[d](Weight of polymer precipitated —Weight of prepolymer) / Weight of monomer charged) × 100.
[e]Original product without solvent fractionation.
[f]Soxhlet extraction with proper solvent.

Block Copolymer			Composition (styrene / MMA)		DF
Polymer	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	by ^{1}HNMR	by GPC	
XPMMA-b-PST-b-PMMA	17,100	1.49	29 / 142	29 / 137	1.78

the relative ratio of methoxy proton (f) at 3.72 ppm of the MMA unit and phenyl protons ((h) and (g)) at 6.3–7.2 ppm of the styrene unit, the composition of the block copolymer was 17.0% polystyrene and 83.0% poly(MMA). These values agree with those obtained by GPC measurement in Table 1. Moreover, the DF was obtained from the peak intensity ratios of the *tert*-butyl proton (b) at 1.27 ppm, though it is weak to the methoxy proton (f) at 3.72 ppm, and is estimated to be 1.78. This value also agreed with that of **XPST1** as a starting polymeric photoiniferter. It revealed that the undesired reaction did not occur during in this block copolymerization. On the other hand, the ^{1}H NMR spectrum of the homo poly(MMA) is shown in Figure 7 (C). From the signals of methyl group (a') at 0.91, 1.05, and 1.22 ppm, the tacticity of poly(MMA) was estimated as rr/mr(rm)/mm: 65/30/5. These values are very close to those of the one prepared using a typical radical initiators [13].

It is clear that the ABA type triblock copolymer of styrene and MMA, **XPMMA-b-PST-b-PMMA**, can be prepared successfully using a **XPST1** containing seleno groups at both chain ends as polymeric photoiniferter. From the above viewpoint, it is seen that a ABA type triblock copolymer of poly(MMA) core can be prepared from block copolymerization of styrene using a telechelic poly(MMA) containing seleno group at both chain ends as polymeric photoiniferter. The further study for comparison of the chemical and physical properties of two types compounds are in progress, and it will be reported in the near future.

Synthesis of ABA Type Triblock Copolymer of Styrene and *p*-Chloromethylstyrene

In analogy to the above method, the block copolymer of styrene with CMS was prepared from **XPST2** ($\overline{M}_n$ = 2,200, $\overline{M}_w / \overline{M}_n$ = 1.62, DF = 2.20) as a polymeric photoiniferter as shown in Equation 3. Here, DF is beyond 2.0 due to the residue of unreacted **XBTSE** as shown in Figure 9 (C). The methenes signal, due to **XBTSE** at 4.05 ppm, differ from methenes signal in core of polystyrene at 3.72 ppm was an indication. On the other hand, the results of block copolymerization is shown in Table 2. No solvent combination that would separate block copolymers and homopolymers completely is presently available. However, GPC and ^{1}H NMR analysis revealed that the ABA type triblock copolymer, **XPCMS-b-PST-b-PCMS**, was prepared in accordance with our expectations. First, the curve of **XPCMS-b-PST-b-PCMS** was shifted to a higher molecular weight region in comparison with **XPST2** in Figure 8. This curve unimodal in GPC curve, and the $\overline{M}_w / \overline{M}_n$ was almost unchanged compared to that of **XPST2** (1.43–1.62). Next, the DF was obtained from comparing the $\overline{M}_n$ by GPC with the peak intensity ratio of *tert*-butyl signal at 1.27 ppm to methylene signals at 4.52 ppm was calculated to be 1.82 in Figure 9 (B). Furthermore, the same value was obtained from the peak intensity ratio of *tert*-butyl signal at 1.27 ppm to sum of methine and methylene signals of polymer backbone at 1.4–2.6 ppm. These values were also consistent

XPST2 + $j+k$ CH$_2$=CH—⟨C$_6$H$_4$⟩—CH$_2$Cl $\xrightarrow{\ \text{h}\,\nu\ }$

XPCMS-b-PST-b-PCMS (3)

$\xrightarrow{\ \text{h}\,\nu\ }$ $h+i$ CH$_2$=CH—⟨C$_6$H$_4$⟩—CH$_3$

XPMS-b-PCMS-b-PST-b-PCMS-b-PMS (4)

Table 2. Preparation of ABA Type Triblock and Multiblock Copolymer of Styrene and *p*-Substituted Styrene[a,a]

Polymer	Prepolymer			Time (h)	Total yield[c] (g)	Conversion[d] of CMS (%)	ABA Triblock Copolymer				Composition (styrene / CMS)	
	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	DF[b]				Polymer	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	DF	by ^{1}HNMR	by GPC
XPST2	2,200	1.62	2.20	25	0.54	23.2	**XPCMS-b-PST-b-PCMS**	3,800	1.43	1.82	17 / 9	17 / 10

[a]Conditions : 0.95 mL of CMS, 0.3 g of prepolymer (**XPST2**), and 1 mL of benzene were irradiated, [**XPST2**]/[CMS] = 0.02.
[b]DF was obtained from GPC and ^{1}HNMR analysis.
[c]Weight of polymer precipitated with methanol (gross polymer).
[d](Weight of polymer precipitated—Weight of prepolymer) / Weight of monomer charged) × 100.

Polymer	Prepolymer			Time (h)	Total yield (g)	Conversion of MS (%)	Multiblock Copolymer				Composition (styrene / CMS / MS)	
	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	DF				Polymer	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	DF	by ^{1}HNMR	by GPC
XPCMS-b-PST-b-PCMS	3,800	1.43	1.82	24	0.23	21.1	**XPMS-b-PCMS-b-PST-b-PCMS-b-PMS**	7,600	2.54	2.10	17 / 9 / 28	17 / 10 / 32

[a]Conditions : 0.7 mL of MS and 0.1 g of prepolymer (**XPCMS-b-PST-b-PCMS**) were irradiated, [**XPCMS-b-PST-b-PCMS**] / [MS] = 0.005.
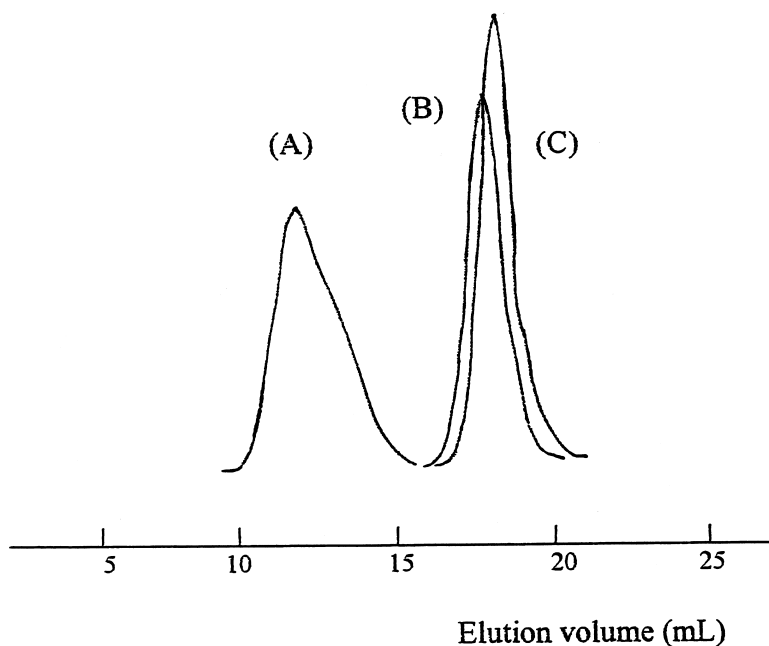
Figure 8. GPC profiles of (A) **XPMS-b-PCMS-b-PST-b-PCMS-b-PMS** ($\overline{M}_n$ = 7,600, $\overline{M}_w/\overline{M}_n$ = 2.54), (B) **XPCMS-b-PST-b-PCMS** ($\overline{M}_n$ = 3,800, $M_w/\overline{M}_n$ = 1.43), and (C) **XPST2** ($\overline{M}_n$ = 2,200, $M_w/\overline{M}_n$ = 1.62).

with that of **XPST2**. On the other hand, approximate composition of the block copolymer was determined from by comparing the relative ratio of methylene protons (e) in para site of CMS unit and phenyl protons at 6.1–7.4 ppm of the sum of styrene and CMS units. The value (17/9) agree with that obtained by GPC measurement (17/10). From the above results, the **XPST2** would function as polymeric photoiniferter for the polymerization of CMS to afford the corresponding ABA type block copolymer.

Synthesis of Multiblock Copolymer of Styrene and p-Substituted Styrenes

Photopolymerization of MS with ABA type triblock copolymer of styrene and CMS (**XPCMS-b-PST-b-PCMS**, $\overline{M}_n$ = 3,800, $\overline{M}_w/\overline{M}_n$ = 1.43, numbers of styrene and CMS units are 17 and 10, respectively) as polymeric photoiniferter in benzene was carried out as shown in Equation 4. The result is also shown in Table 2. A multiblock copolymer (**XPMS-b-PCMS-b-PST-b-PCMS-b-PMS**) was obtained with $\overline{M}_n$ = 7,600, $\overline{M}_w/\overline{M}_n$ = 2.54 by GPC in Figure 8(A). This curve was bimodal and shows the number of PMS unit is 32. But, $\overline{M}_w/\overline{M}_n$ was increased than that of **XPCMS-b-PST-b-PCMS**. This multiblock copolymer involving small amounts of homopolymers of MS is thus due to photopolymerization. Figure 9
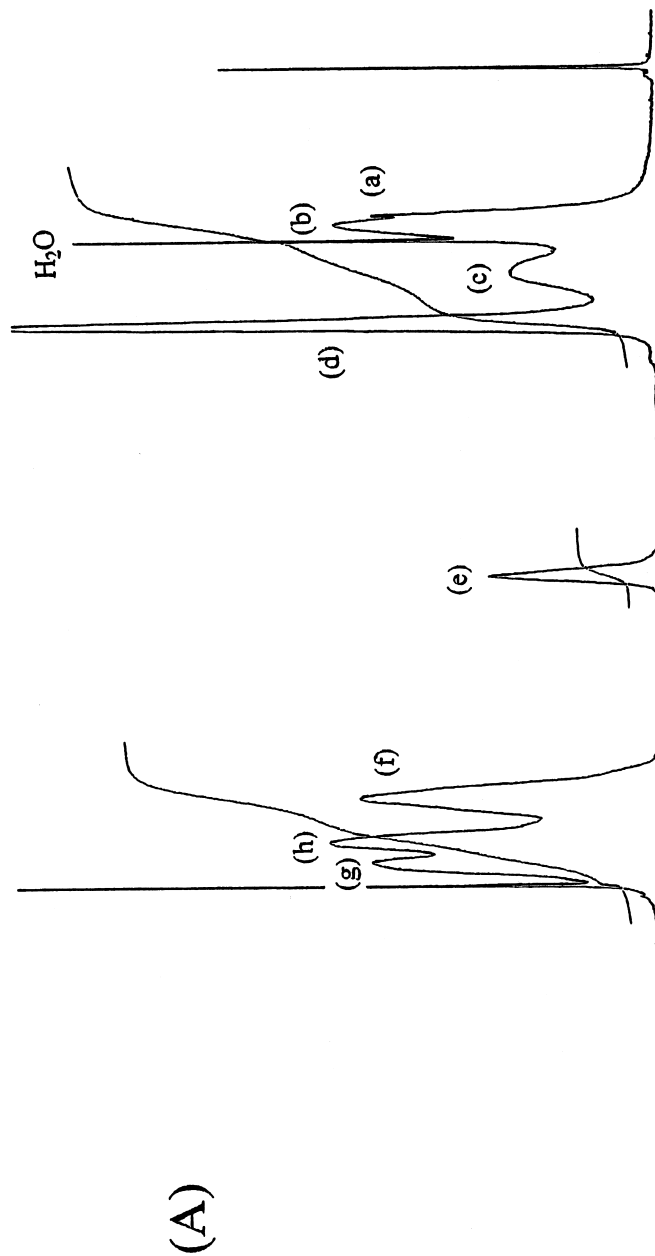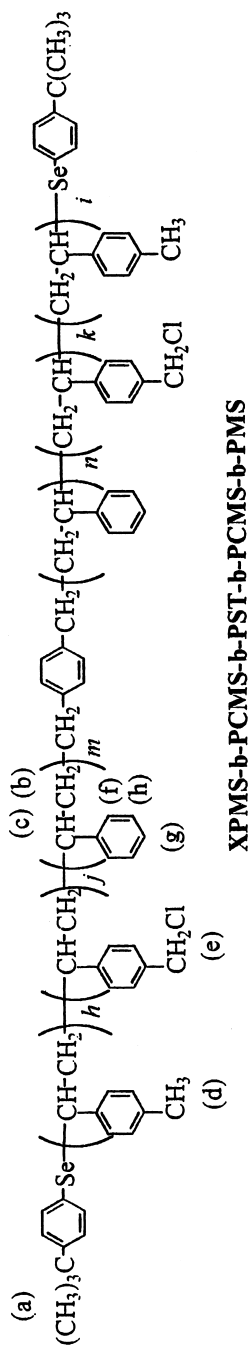
Figure 9. ^{1}H NMR spectra (200MHz, in CDCl$_3$) of (A) **XPMS-b-PCMS-b-PST-b-PCMS-b-PMS** ($\overline{M}_n$ = 7,600, $\overline{M}_w /\overline{M}_n$ = 2.54), (B) **XPCMS-b-PST-b-PCMS** ($\overline{M}_n$ = 3,800, $\overline{M}_w /\overline{M}_n$ = 1.43), and (C) **XPST2** ($\overline{M}_n$ = 2,200, $\overline{M}_w /\overline{M}_n$ = 1.62).
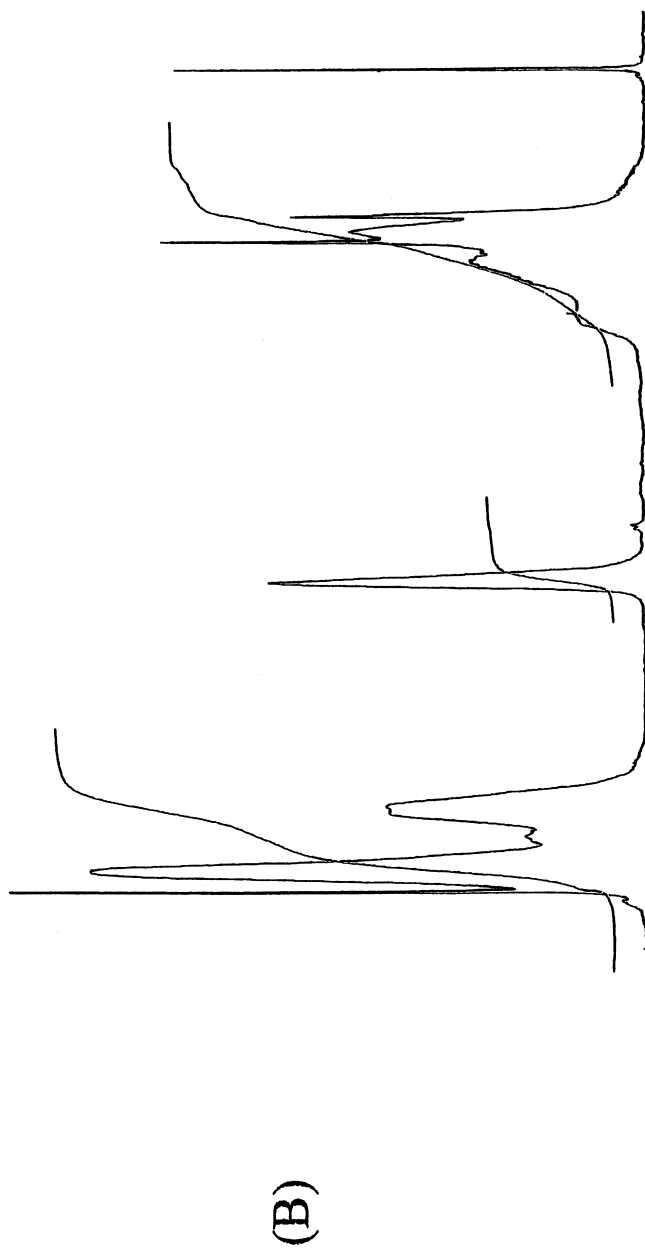
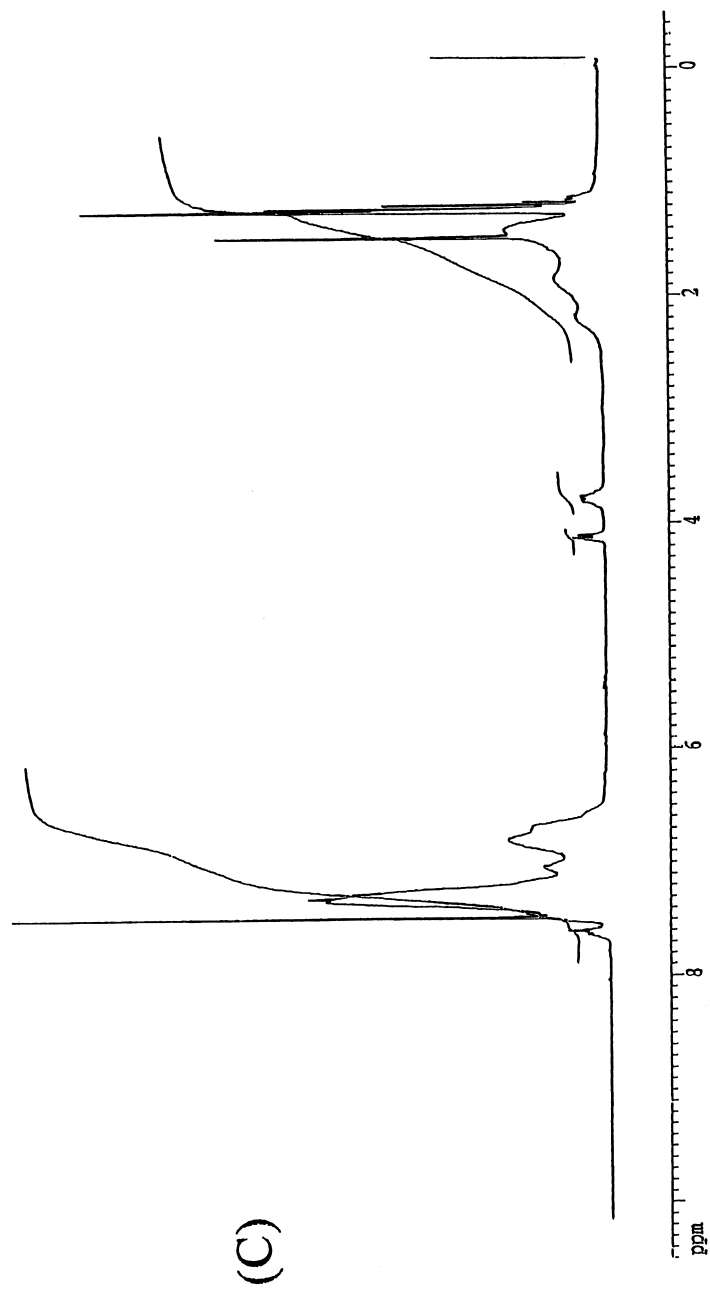(B)

Figure 9. Continued

(C)

Figure 9. Continued

(A) shows the ^{1}H NMR spectrum of **XPMS-b-PCMS-b-PST-b-PCMS-b-PMS**. Determination of DF in multiblock copolymer by *tert*-butyl signal was difficult because of the very low concentration of the end groups. DF was obtained from comparing the $\overline{M}_n$ by GPC with the peak intensity ratio of a *tert*-butyl signal at 1.27 ppm to methyl signal at 2.3 ppm was calculated to be 2.1. On the other hand, by comparing the intensity ratios of methyl proton (d) at 2.3 ppm of the MS and phenyl protons (f, g, and h) at 6.1–7.4 ppm, the numbers of St, CMS, and MS units in were obtained 17, 9, and 28, respectively. These values approximately agree with that of obtained by GPC (17/10/32). These results revealed that ABA type triblock copolymer functioned as polymeric photoiniferter, and it should be possible to obtain the multiblock copolymer of styrene and *p*-substituted styrenes.

CONCLUSION

1,4-Bis(*p-tert*-butylphenylselenomethyl)benzene was used as a bifunctional photoiniferter for the polymerization of methyl methacrylate. Photoirradiation of telechelic polystyrene having phenylseleno groups as polymeric photoiniferter in the presence of methyl methacrylate or *p*-chloromethyl styrene afforded effectively corresponding to the ABA type triblock copolymers. On the other hand, photoirradiation of resulting ABA type triblock copolymer as polymeric photoiniferter with *p*-methyl styrene afforded effectively multiblock copolymer of styrene and *p*-substituted styrenes.

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