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SYNTHESIS OF DIBLOCK COPOLYMERS BY END FUNCTIONAL POLYSTYRENE CONTAINING PHENYLSELENO GROUPS AS POLYMERIC PHOTOINIFERTER

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ABSTRACT

Block copolymers of styrene and *p*-substituted styrene were prepared by photopolymerization of *p*-bromostyrene or *p*-methylstyrene in the presence of end functional polystyrene (**DPDSE-PST**) containing phenylseleno groups at the α and ω-chain ends as polymeric photoiniferter. To determine the form of resulting block copolymers, the behavior of chain terminals of **DPDSE-PST** was investigated. The ability of photoinitiate and chain transfer of β-phenylethyl *p*-*tert*-butylphenyl selenide as a model compound of α-chain end of **DPDSE-PST** was much smaller than that of benzyl phenyl selenide as a model compound of ω-chain end of **DPDSE-PST**. On the other hand, the polymerization of styrene, prepared by 1,4-Bis(*p*-*tert*-butylphenyl) diselenide as photoiniferter, with styrene also revealed a form of the resulting block copolymer was an AB block structure.

Key Words: Diphenyl diselenide; β-Phenylethyl *p*-*tert*-butylphenyl selenide; 1,4-Bis(*p*-*tert*-butylphenyl) diselenide; Radical polymerization; Photoiniferter; Polymeric photoiniferter; Block copolymer

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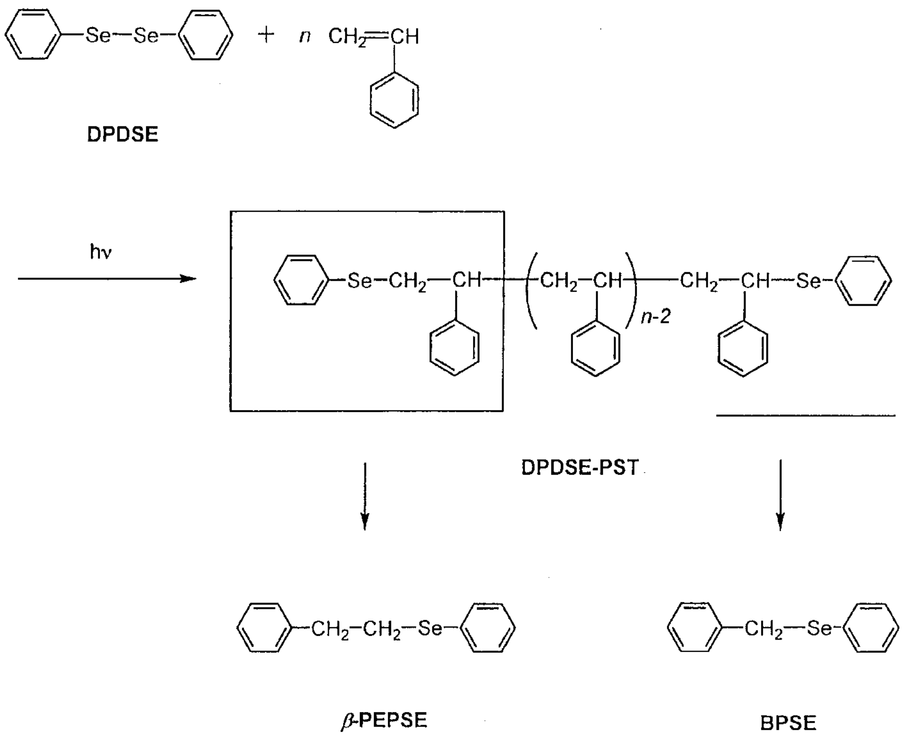
INTRODUCTION

Preparation of well-defined block copolymers by radical polymerization has attracted much attention because of their widespread applications in fields of surfactants, adhesives, fibers, elastomers, etc. Several methods have been reported for the synthesis of well-defined block copolymers.[1–7] Among them, the photoiniferter technique has been one of the techniques well known as a simple procedure, and a variety of monomers can be applied. For instance, the AB or ABA type block copolymers were prepared by the radical polymerization of vinyl monomer in the presence of dithiocarbamyl end functional polymer under photoirradiational conditions.[8–11]

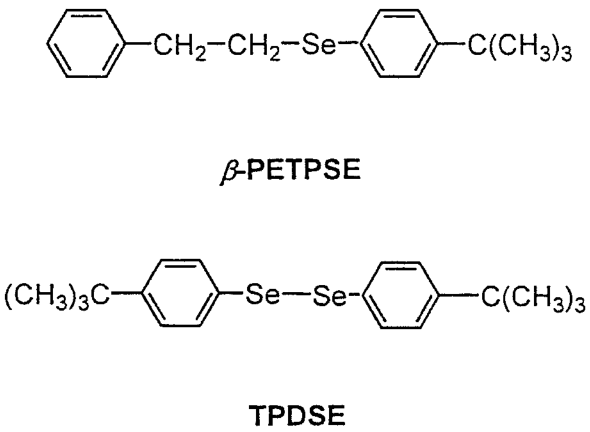
We have already reported the very high radical capturing ability of diphenyl diselenide (DPDSE) in photopolymerization of styrene.[12] On the basis of this fact, we could be obtained the polystyrene (**DPDSE-PST**) having phenylseleno groups at both chain ends. Furthermore, it turned out that α-and ω-chain end of **DPDSE-PST** were different structure, such as β-phenylethyl phenylselenide (**β-PEPSE**) and benzylphenyl selenide (**BPSE**), respectively (Sch. 1). We also reported a photopolymerization of styrene in the presence of BPSE as a model compound of ω-chain end of **DPDSE-PST**.[13] The resulting polystyrene (BPSE-PST) containing benzyl and phenylseleno groups at α-and ω-chain ends, respectively, was obtained from this method. Moreover, BPSE-PST as a polymeric photoiniferter affords a well-defined block copolymer of styrene with methyl methacrylate or *p*-substituted styrenes.[14]

From ^{1}H NMR and GPC analysis, it was proved that block copolymerization proceeded by insertion of second monomer into carbon and selenium bonds at ω-chain end of **BPSE-PST**. Therefore, the resulting block copolymers were ascertained to be formed AB or ABC type block structure. From this viewpoint, we thought that block copolymerization by **DPDSE-PST** as polymeric photoiniferter proceeds differently from that of **BPSE-PST**. In fact, the photocleavage of sp^3 carbon and selenium bond at α-terminal cannot be ignored completely since even an alkyl selenide as model compound of α-terminal group have been found to dissociate on UV irradiation.[15] Unfortunately, however, the behavior of the α-chain end of **DPDSE-PST** has not been reported until now.

This paper describes the synthesis of block copolymer of styrene with *p*-bromostyrene (**BS**) or *p*-methylstyrene (**MS**) by photoiniferter method with **DPDSE-PST**. Further, investigation for the form of resulting block copolymers by behavior of β-phenylethyl *p*-*tert*-butylphenyl selenide (**β-PETPSE**) as a model compound of α-chain end of **DPDSE-PST** is also reported. Here, the *tert*-butyl group is employed because it is easily confirmed in ^{1}H NMR spectrum (Sch. 2).



Scheme 1.



Scheme 2.

EXPERIMENTAL

Materials

Styrene and **MS** were purified by the ordinary method and distilled in a stream of nitrogen just before use. **BS** was prepared as in previous paper.[14] **DPDSE** and 1,4-bis(*p*-*tert*-butylphenyl) diselenide (**TPDSE**) were prepared according to the previous paper.[16] Solvents were purified by distillation after appropriate drying. Other reagents were obtained commercially and used without further purification.

Synthesis of β-PETPSE

Selenium powder (7.11 g, 0.09 mol) was added gradually over 30 m to a solution of 4-*tert*-butylphenylmagnesiumbromide prepared from magnesium (2.43 g, 0.1 mol) and 1-bromo-4-*tert*-butylbenzene (21.31 g, 0.1 mol) in THF (55 mL), and refluxed for additional 1 h. Then, to this reaction mixture, (2-bromoethyl) benzene (16.66 g, 0.09 mol) was added slowly, and the mixture was further stirred at room temperature for 1 h. A solution of ammonium chloride in water (150 mL, 2.88 mol/L) was added to the reaction mixture, and the product was extracted with diethyl ether and dried over anhydrous sodium sulfate. After evaporation of solvent, the residue was separated with column chromatography (Wakogel C-200, *n*-hexane) resulting in **β-PETPSE** as an oily compound. The yield was 6.40 g (22.4%).

^{1}H NMR (in $CDCl_3$): $\delta = 1.30$ (s, $C(CH_3)_3$, 9H), 2.90–3.20 (m, $2CH_2$, 4H), 7.15–7.50 ppm (m, C_6H_5, SeC_6H_4, 9H)

Analysis. Calculated for $C_{18}H_{22}Se$: C, 68.13%; H, 6.99%. Found: C, 68.07%; H, 7.01%.

Synthesis of End Functional Polystyrenes (DPDSE-PST or TPDSE-PST1) as Polymeric Photoiniferters

A solution of DPDSE (136 mg) and styrene (5 mL) 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 16 h. The tube was opened and contents were poured into methanol. **DPDSE-PST** was reprecipitated from chloroform to methanol. (Yield, 1.43 g, 31.6%). On the other hand, TPDSE-PST1 (Yield, 0.18 g, 4.0%) was prepared from TPDSE (18.5 mg) with styrene (5 mL) under photoirradiated for 2 h.

Synthesis of Block Copolymers

A solution of **DPDSE-PST** (0.1 g), **BS** or **MS** (3 mL), and benzene (2 mL) in Pyrex tube was irradiated with a high-pressure mercury lamp at room temperature for 10 or 20 h, respectively. The polymer mixture was poured into methanol. The fraction of the polymer was confirmed by GPC and ^{1}H NMR spectra. The composition of block copolymer of **DPDSE-PST** with **MS** was examined by GPC and ^{1}H NMR. On the other hand, the that of block copolymer of **DPDSE-PST** with **BS** was evaluated from elementary analysis of bromine.

Photopolymerization of Styrene with β-PETPSE

A solution of **β-PETPSE** (5.5 mg) and styrene (2 mL) was immersed in a Pyrex tube. The tube was degassed under vacuum by conventional freeze and thaw, and sealed off under vacuum. All polymerizations were carried out by irradiation with Riko 100 W high pressure mercury lamp from 8 cm distance at room temperature. After a given time, the tube was opened and the contents were poured into a large amount of methanol as poor solvent. The resulting polymers (**β-PETPSE-PST**) were purified by reprecipitation with methylene chloride and methanol followed by drying in vacuum.

Determination of Chain Transfer Constant (C_{tr}) of β-PETPSE for Styrene

The required amounts of **β-PETPSE** with styrene (5 mL, 43.5 mmol) and AIBN (1.6 mg, 0.01 mmol) were charged into a Pyrex tube of 15 mm diameter. The tube was degassed under vacuum by the conventional freeze and thaw technique, and sealed off under vacuum. All polymerizations were carried out at 60°C, and keeping the yield of polymer below 5%. After polymerization, the mixture was poured into a large amount of methanol to precipitate the polymer. The resulting polymer was then reprecipitated from methylene chloride with methanol, followed by drying in vacuum. The $\mathbf{C_{tr}}$ of **β-PETPSE** for styrene was obtained by Mayo's equation (Eq. (1)):[17]

$$1/P_n \fallingdotseq 1/P_o + \mathbf{C_{tr}}[\mathbf{CTA}]/[M] \qquad (1)$$

where P_o and P_n are the degree of polymerization in the absence or presence of the chain transfer agent (**CTA**), respectively.

Synthesis of β-PETPSE-PSO by Oxidative Elimination of β-PETPSE-PST

A solution of **β-PETPSE-PST** (0.2 g) and 30% aqueous hydrogen peroxide (0.05 g) in THF (2 mL) was stirred for 1 week at room temperature. After evaporation of most of THF, the residue was poured into methanol to precipitate polymer. The resulting polymer (**β-PETPSE-PSO**) was purified by reprecipitation from methylene chloride with methanol, followed by drying in vacuum. Yield was 0.19 g (96%).

Photopolymerization of Styrene with TPDSE-PST1 as Polymeric Photoiniferter

Samples of **TPDSE-PST1** (0.1 g) with styrene (1.5 mL) and benzene (1 mL) were charged into polymerization tubes. The solutions were irradiated with high pressure mercury lamp for 10 h at room temperature. The reaction mixtures were poured into methanol. The resulting polymer (**TPDSE-PST2**) were dried in vacuum.

Measurements

^{1}H-NMR spectra were recorded by a JEOL JNM-GX400 (400 MHZ) spectrometer 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. Elementary analysis was carried out with Yanaco CHN CORDER MT-3.

RESULTS AND DISCUSSION

Synthesis of Block Copolymers of DPDSE-PST with MS or BS

Block copolymerization of end functional polystyrene (**DPDSE-PST**, $\bar{M}_n = 3{,}100, \bar{M}_w/\bar{M}_n = 1.62$) with **MS** or **BS** was carried in benzene at room temperature under irradiation condition. No solvent combination that would separate block copolymers and homopolymers is presently available. But as shown in Fig. 1, the peaks in GPC for resulting block copolymers were unimodal, and were shifted to the higher molecular weight region in comparison with **DPDSE-PST** as prepolymer. It reveals that **DPDSE-PST** would function as polymeric photoiniferter for the polymerization of **MS** or **BS** to allow the corresponding block copolymers,

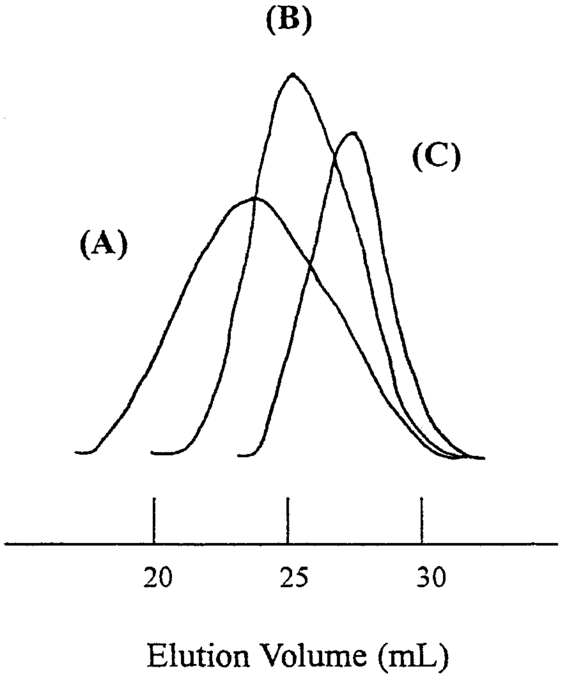
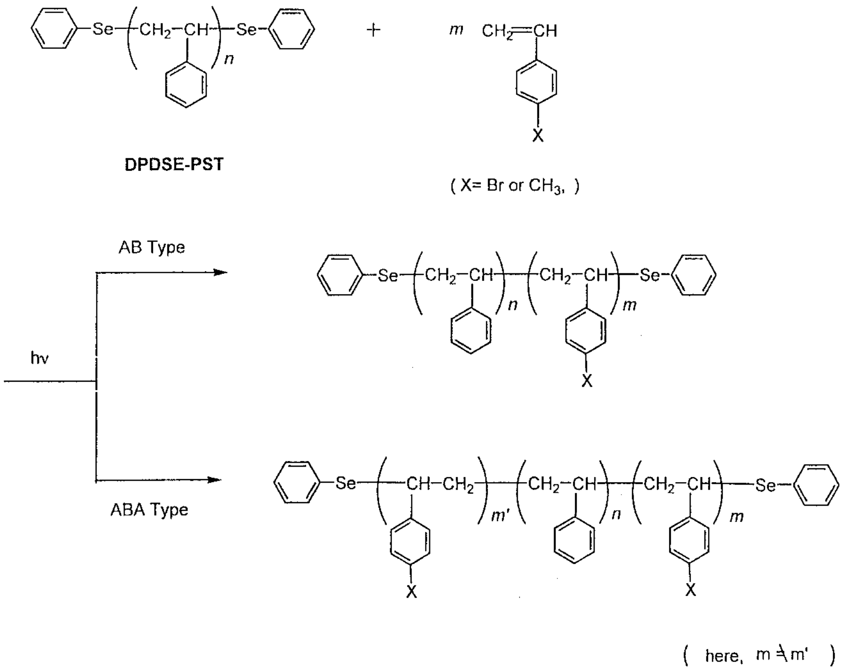


Figure 1. GPC profiles of (A) **DPDSE-PST-b-PBS** ($M_n = 9{,}700, M_w/M_n = 3.77$), (B) **DPDSE-PST-b-PMS** ($M_n = 7{,}000, M_w/M_n = 2.06$), and (C) **DPDSE-PST** as polymeric photoiniferter ($M_n = 3{,}100, M_w/M_n = 1.62$).

DPDSE-PST-b-PMS or **DPDSE-PST-b-PBS**, respectively. The composition of the block copolymers was determined from ^{1}H-NMR spectrum as seen in Fig. 2(B) in case of **DPDSE-PST-b-PMS**. The relative ratio of methyl proton (c) in para site of **MS** unit and phenyl protons (d–f) of the sum of styrene and **MS** unit. The results are shown in Table 1. These values quite agree with those obtained by GPC measurement. The $\bar{M}_w/\bar{M}_n$ of **DPDSE-PST-b-PBS** was very wide as same result of our previous report.[14]

Form of Resulting Block Copolymers

Here, we thought that the form of resulting block copolymers was determined to be caused by the behavior of α-terminal group of **DPDSE-PST**. First, if the α-terminal group of **DPDSE-PST** did not occur in the polymerization, AB type of block copolymer would be obtained according to Eq. (2). Next, if the α-terminal group of **DPDSE-PST** is considered in polymerization, the structure of resulting block copolymer is ABA type (Eq. (3)). Therefore, the form of resulting block copolymers would be proved by investigation for the behavior of **β-PETPSE** as a model compound of α-terminal group of **DPDSE-PST**.



(2)

(3)

Photopolymerization of Styrene with β-PETPSE

To investigate the behavior of **β-PETPSE** in photopolymerization of styrene, the polymerization was carried out on irradiation to a solution of styrene and **β-PETPSE**. The results show in Table 2. Polymerizations proceeded in the presence of **β-PETPSE**, and the yield increased with the increasing amount of **β-PETPSE** and polymerization times. On the other hand, the $\bar{M}_n$ decreased with the increasing amount of **β-PETPSE**. These results reveal that **β-PETPSE** worked as photoinitiator and chain transfer agent at the same time. However, polymer yields and $\bar{M}_n$ values of the resulting polymers were not found to increase with the reaction times, and also, $\bar{M}_n$ values of the resulting polymers were not found to increase with the polymer yields. On the other hand, the resulting polymers have wide values of $\bar{M}_w/\bar{M}_n$. These results suggest that **β-PETPSE** worked as photoiniferter in polymerization of styrene were not effectively. Therefore, it was considered that the chain ends of resulting polymers were not controlled.

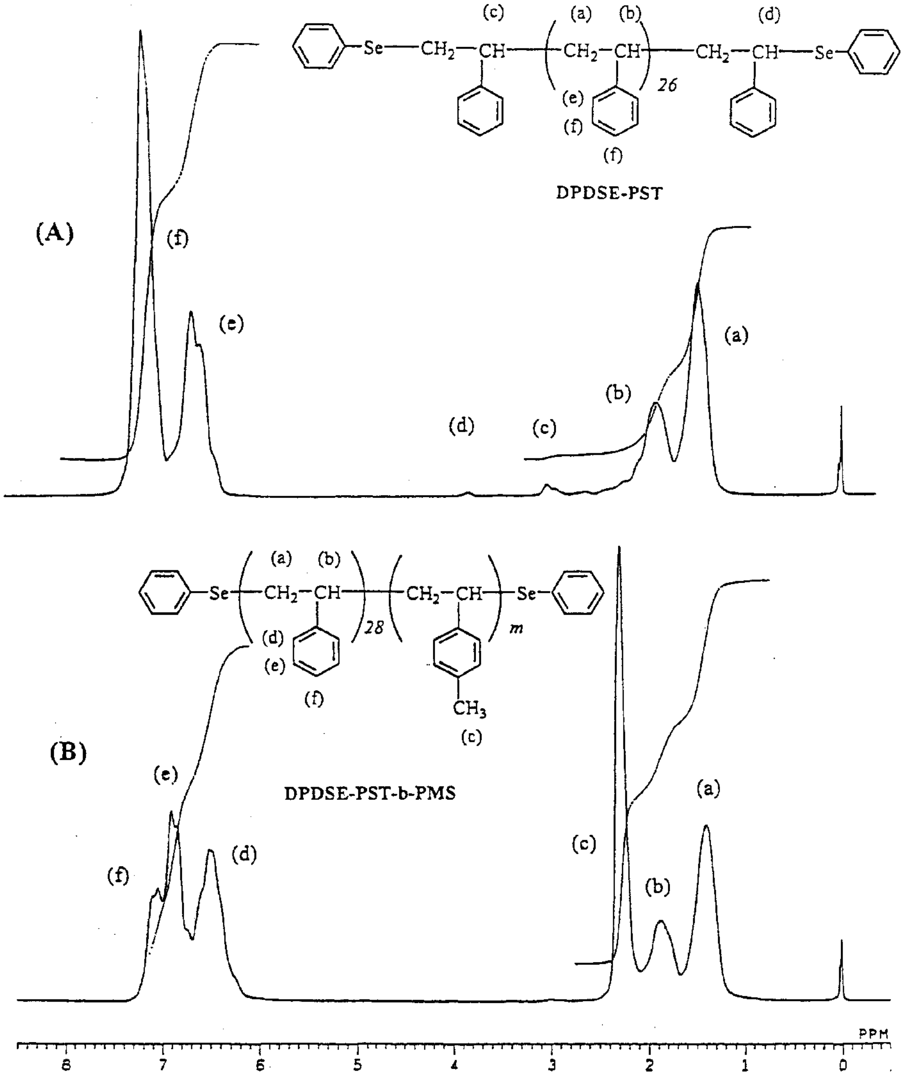


Figure 2. ^{1}H NMR spectra (400 MHz, in $CDCl_3$) of (A) **DPDSE-PST** ($M_n = 3{,}100$, $M_w/M_n = 1.62$) and (B) **DPDSE-PST-b-PMS** ($M_n = 7{,}000$, $M_w/M_n = 2.06$).

Determination of Chain Transfer Constant (C_{tr}) of β-PETPSE for Styrene

To determine the chain transfer ability of **β-PETPSE** for Styrene, polymerization was carried out at 60°C in the presence of AIBN as an initiator. The result is shown in Fig. 3. The C_{tr} was obtained by the slope of this straight line, the value was 0.21. This value is lower than that of **BPSE**[13] as a model compound of ω-terminal end of **DPDSE-PST** in Sch. 1. It reveals that the ability of radical capturing and terminal control in polymer main chain of **β-PETPSE** is lower than that of **BPSE**.

Table 1. Preparation[a] of Block Copolymers from **DPDSE-PST**[b] with *p*-Substituted Styrene (M_2)

					Degree of Polymerization of Block Copolymer		
	Time	Yield[d]			by ^{1}H NMR[e]	by GPC	by Br Analysis
Block Copolymer[c]	h	%	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Styrene : M_2	Styrene : M_2	Styrene : M_2
DPDSE-PST-b-PMS	20	10.1	7,000	2.06	28 : 37	28 : 33	
DPDSE-PST-b-PBS	10	25.0	9,700	3.77		28 : 36	28 : 45

[a] Irradiation of 100 W high pressure mercury lamp at room temperature; [b] **DPDSE-PST** (Polymeric photoiniferter), 0.1 g, $\bar{M}_n = 3{,}100$, $\bar{M}_w/\bar{M}_n = 16.2$; [c] 23.0 mmol of *p*-Substituted styrene in benzene (2 mL) solution. [**DPDSE-PST**]/[M2] = 0.002; [d] Yield (%) = ((Weight of precipitated polymer − Weight of prepolymer) / Weight of charged monomer) × 100, that is conversion of *p*-substituted styrene; [e] 400 MHz in $CDCl_3$.

Determination of Structure of Chain Terminal of β-PETPSE-PST

The resulting polystyrene chain ends structure (**β-PETPSE-PST**, $\bar{M}_n = 4{,}200$, $\bar{M}_w/\bar{M}_n = 1.44$) which was prepared from polymerization of styrene with **β-PETPSE** as photoiniferter under irradiation condition was investigated by the analysis of ^{1}H NMR spectrum. In order to accurately determine the chain terminal structure polystyrene having low $\bar{M}_n$ values was required. Figure 4 is shows the ^{1}H NMR spectrum of **β-PETPSE-PST**. Two

Table 2. Photopolymerization of Styrene in the Presence of **β-PETPSE**

Run	[**β-PETPSE**]/[styrene][a]	Time (h)	Yield[b] (%)	$\bar{M}_n^c$	$\bar{M}_w/\bar{M}_n$
1	0	10	2.9	66,000	4.01
2	0.001	4	3.1	12,500	1.83
3	0.001	12	8.1	13,100	2.11
4	0.001	16	11.7	12,500	2.17
5	0.001	20	13.0	15,300	2.32
6	0.001	24	16.3	15,300	2.35
7	0.01	4	8.3	9,900	1.60
8	0.01	12	22.9	7,900	1.98
9	0.01	16	26.0	10,300	1.93
10	0.01	20	33.2	9,200	2.01
11	0.01	24	36.7	10,800	2.04

[a] Styrene = 5 mL; [b] Recovery of polymer which was insoluble part to methanol. [c] Estimated by GPC.

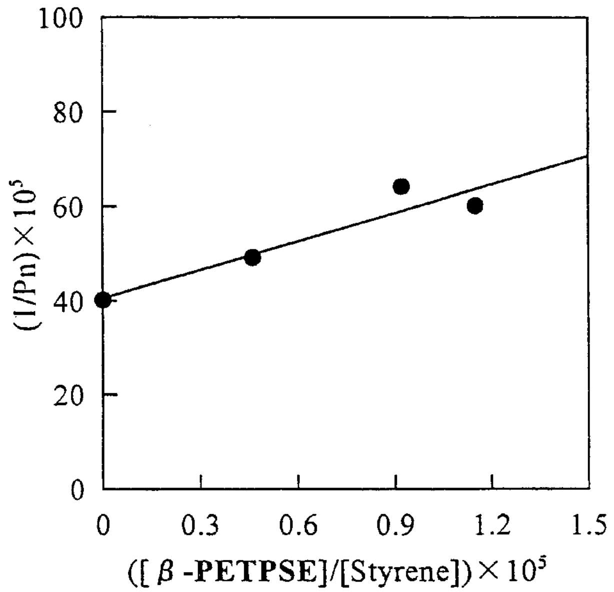
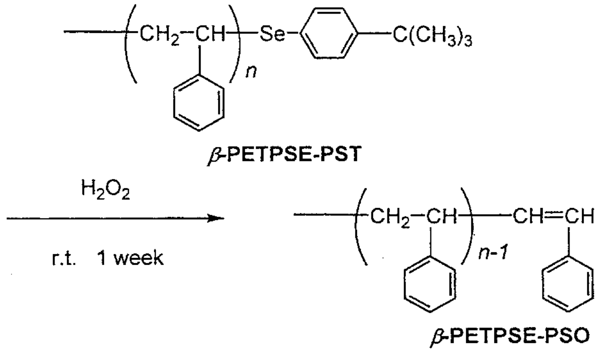


Figure 3. The Mayo plot for the polymerization of styrene with **β-PETPSE**. [styrene] = 43.5 mmol. [AIBN] = 0.01 mmol.

signals due to *t*-butyl group appeared at $\delta = 1.27$ and 1.30 ppm in this spectrum; this suggest the presence of the two kinds of *t*-butyl group, which were assigned to the α-chain terminal group as well as ω-chain terminal group. Further, it was found that at least over 82% of polystyrene having a phenylseleno group at both chain ends exist in **β-PETPSE-PST** from the peak intensity ratio of (c) to (d).

This fact was also confirmed by the elimination of phenylseleno group in chain ends of **β-PETPSE**-PST (Eq. (4)). Figure 5 is shows the ^1H NMR spectrum of **β-PETPSE**-PSO. As seen in this spectrum, two signals of *t*-butyl group at $\delta = 1.27$ and 1.30 ppm completely disappeared and appeared the



(4)

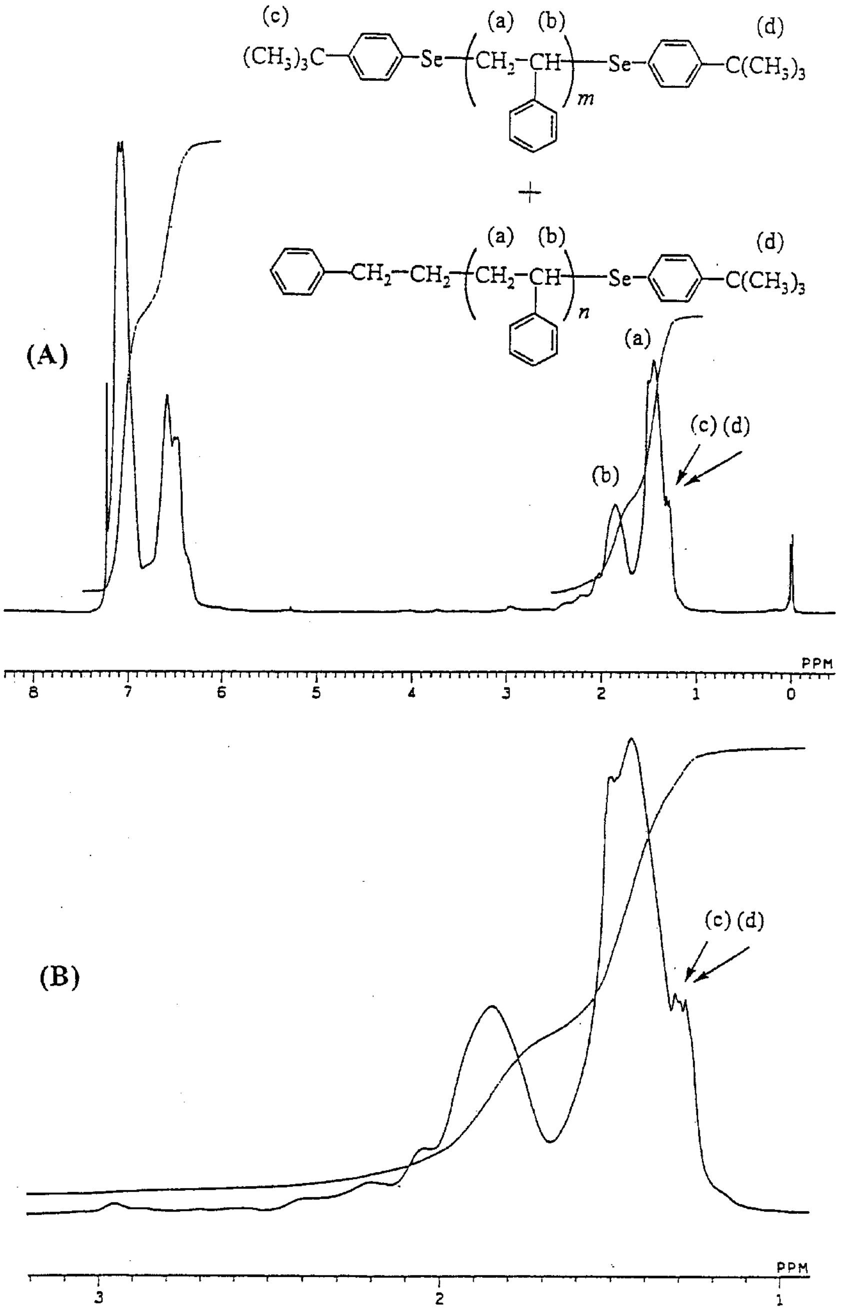


Figure 4. ^{1}H NMR spectra (400 MHz, in $CDCl_3$) of **β-PETPSE-PST** ($M_n = 4{,}200$, $M_w/M_n = 1.44$).

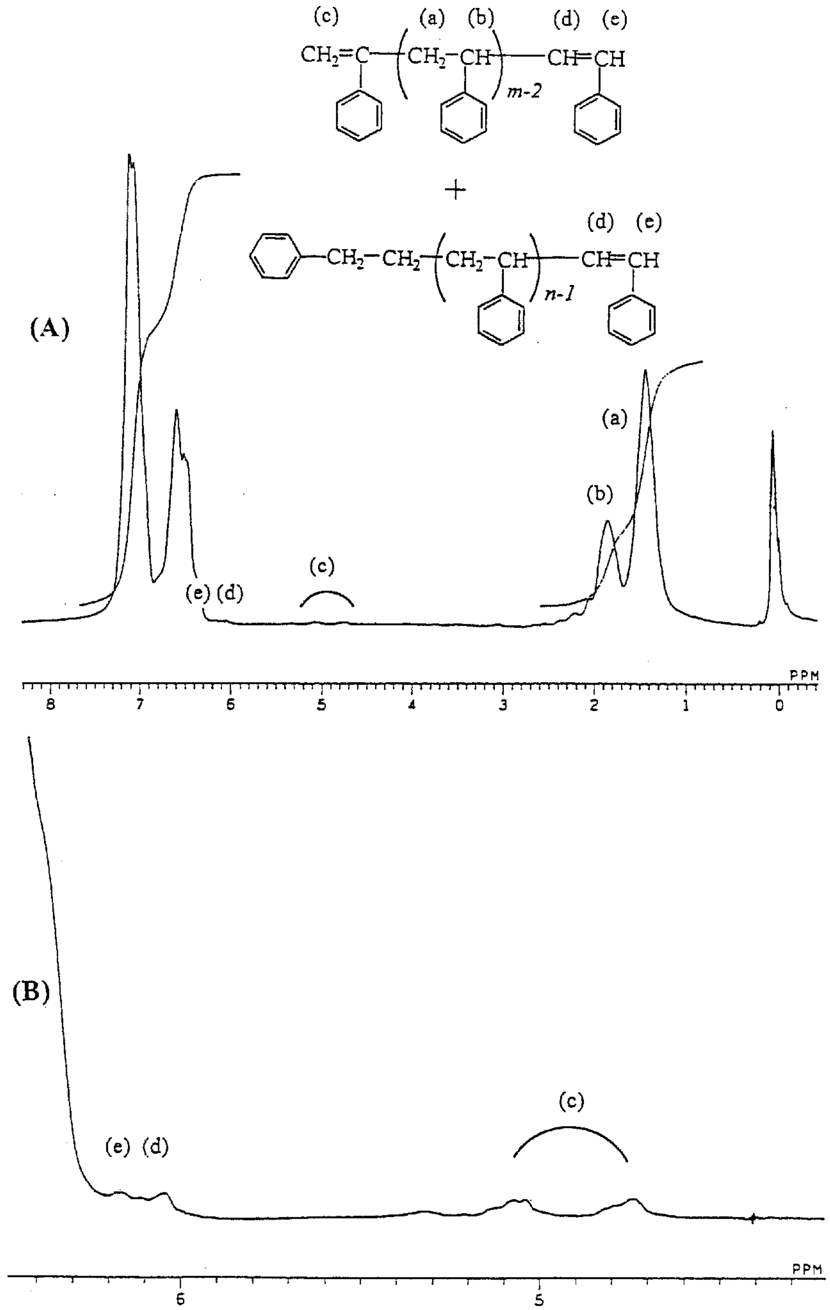


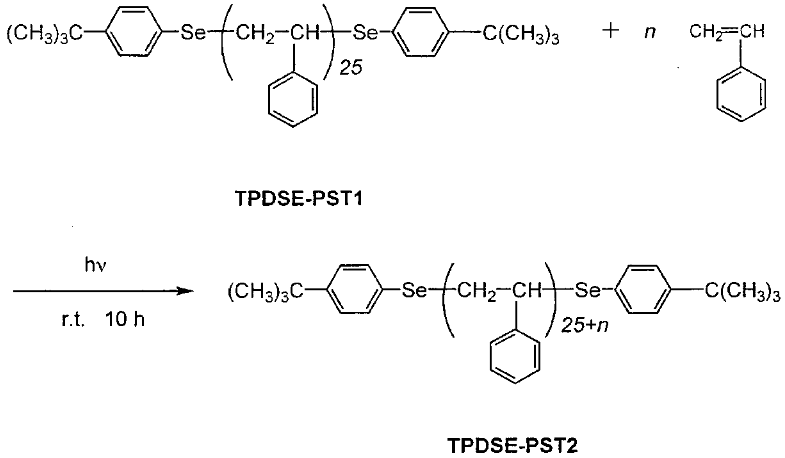
Figure 5. ^{1}H NMR spectra (400 MHz, in $CDCl_3$) of **β-PETPSE-PSO** ($M_n = 4{,}000$, $M_w/M_n = 1.43$).

signals of vinyl protons at $\delta = 4.75$ and 5.07 ppm and vinylene protons at 6.03–6.20 ppm. This result also indicates that the **β-PETPSE**-PSO has different structures at the α-chain end.

Photopolymerization of Styrene with TPDSE-PST1 as Polymeric Photoiniferter

The behavior of chain terminal groups of **DPDSE-PST** was investigated by another method. Polymerization of styrene with the end functional polystyrene (TPDSE-PST1, $\bar{M}_n = 4,200, \bar{M}_w/\bar{M}_n = 1.44$) as polymeric photoiniferter was carried out under irradiation condition (Eq. (5)). The difference of the peak intensity ratio of two signals of *t*-butyl group at $\delta = 1.27$ and 1.30 ppm in Fig. 6(A) and (B) was hardly discernible. If the styrene monomer insert to between main chain and phenylseleno group in α-chain terminal, a signal of *t*-butyl group at $\delta = 1.27$ ppm should be appeared. This result also shows that the α-chain terminal of polystyrene is hardly concerned in this polymerization.

From the above results, in photopolymerization of styrene in the presence of **DPDSE** as a photoiniferter, polymerization procedure is mainly performed in the ω-chain end, although a few proportions are carried out in α-chain end. Therefore, it is shown that the resulting block copolymer is obtained as a AB type according as Eq. (2) when photopolymerization of **MS** or **BS** in the presence of **DPDSE-PST** as polymeric photoiniferter.



(5)

CONCLUSION

Block copolymers were obtained by photopolymerization with end functional polystyrene (**DPDSE-PST**), prepared by diphenyl diselenide as a

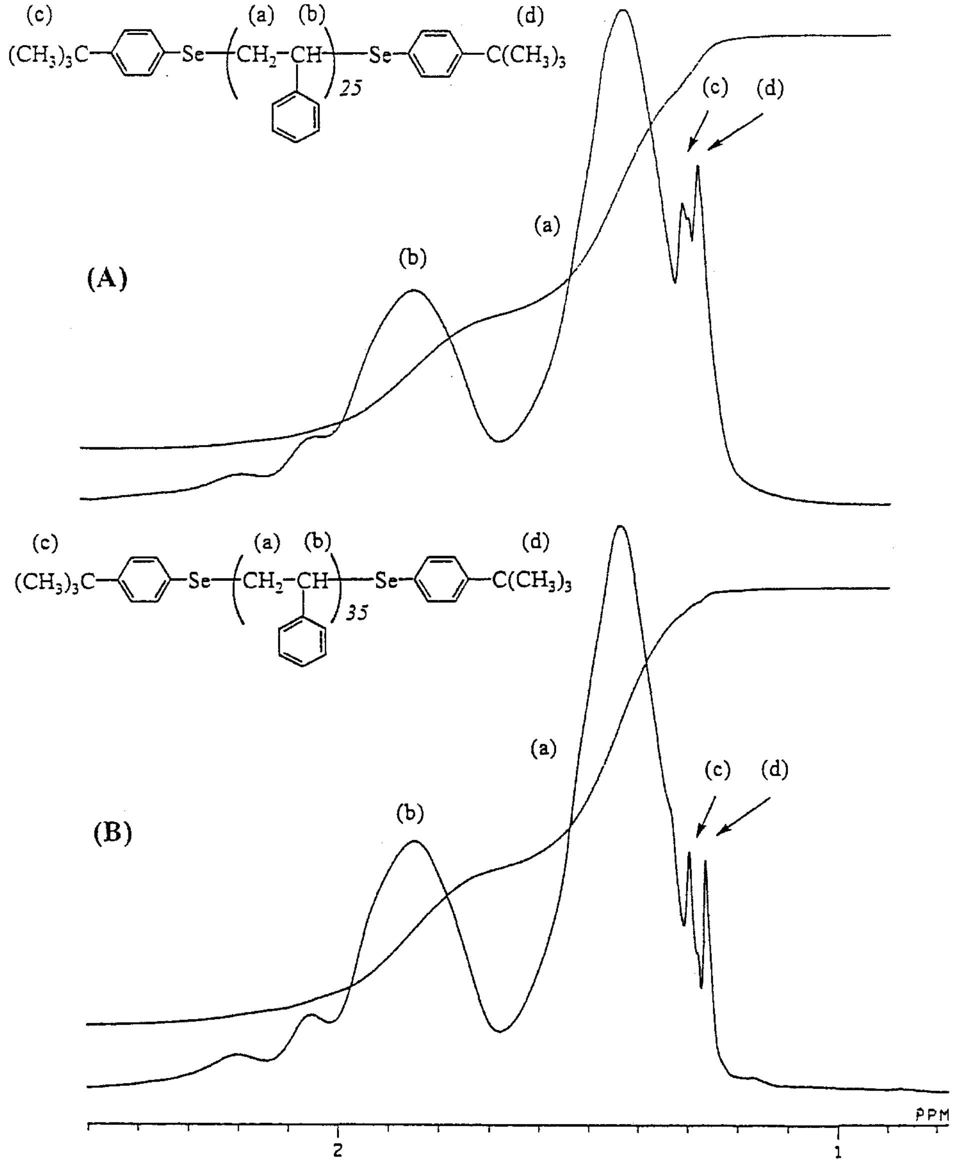


Figure 6. ^{1}H NMR spectra (400 MHz, in $CDCl_3$) of (A) **TPDSE-PST1** ($M_n = 2{,}900$, $M_w / M_n = 2.33$) and (B) **TPDSE-PST2** ($M_n = 3{,}900$, $M_w/M_n = 2.90$).

photoiniferter, in the presence of *p*-bromostyrene or *p*-methylstyrene. Photopolymerization of styrene with β-phenylethyl *p*-*tert*-butylphenyl as model compound of the α-chain end of **DPDSE-PST** and post polymerization of styrene in the presence of polystyrene as polymeric photoiniferter, prepared by 1,4-Bis(*p*-*tert*-butylphenyl) diselenide, were revealed that the form of resulting block copolymers were AB block structure.

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