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Synthesis of Telechelic Polystyrene by Radical Polymerization Using 1,4-Bis(*p-tert*-Butylphenylseleno-Methyl)benzene as a Photoiniferter

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SYNTHESIS OF TELECHELIC POLYSTYRENE BY RADICAL POLYMERIZATION USING 1,4-BIS(*p-tert*-BUTYLPHENYLSELENOMETHYL)BENZENE AS A PHOTOINIFERTER

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Key Words: 1,4-Bis(*p-tert*-butylphenylselenomethyl)benzene, Bifunctional Photoiniferter, Living-like Polymerization, Telechelic Polystyrene

ABSTRACT

1,4-Bis(*p-tert*-butylphenylselenomethyl)benzene was synthesized, and used as a bifunctional photoiniferter for the polymerization of styrene. Both the polymer yields and the number average of molecular weights (${}_n$) of polymers increased with the polymerization. The polymerization of styrene by this iniferter permitted telechelic polystyrene containing arylseleno groups at both chain ends, and the degree of functionality was 1.9. The seleno groups of both chain ends of polystyrene were reduced quantitatively by tri-*n*-butyltin hydride. These seleno groups in polystyrene were also eliminated by treatment with hydrogen peroxide to give telechelic polystyrene with carbon-carbon double bond at both chain ends. Further, polystyrene with double bonds was converted to telechelic polystyrene carrying

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†Deceased August 5, 1997

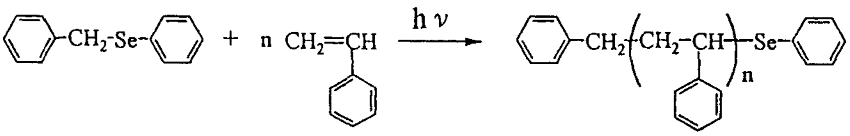
terminal functional groups as epoxy, hydroxy, and iodide group, respectively.

INTRODUCTION

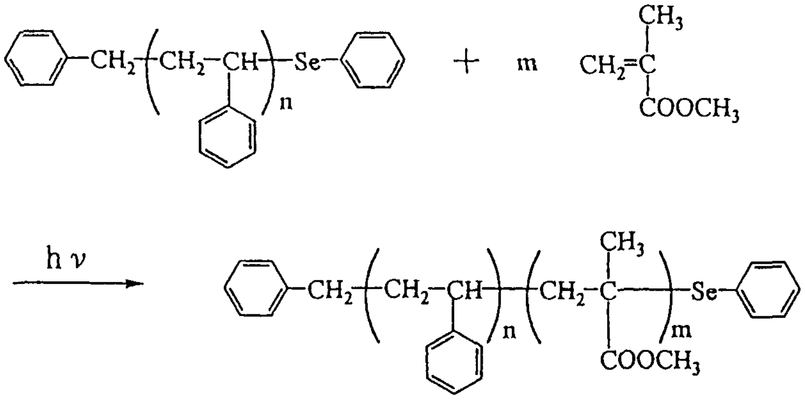
Telechelic polymers are becoming increasingly important for the synthesis of various polymer materials and of novel block and graft copolymers [1]. Conventionally, several methods have been used to prepare telechelic polymers including anionic [2-3], cationic [4, 5], group transfer [6] and radical [7-11] polymerizations. Among them, the preparation of telechelic polymer by radical polymerization with iniferter has been well known as one of the most convenient methods. For example, Otsu *et al.* [12] reported that some dithiocarbamate derivatives as iniferters in photopolymerization of styrene and methyl methacrylate yield polymers contain fragments of the iniferter at both chain ends. Especially, they found that xylylene bis(N,N-diethyldithiocarbamate) was effective bifunctional photoiniferter for synthesis of telechelic polymer [13-15].

On the other hand, organoselenium compounds have been noteworthy as useful tools in organic synthesis [16-20]. In particular, the removal of phenylseleno group occurs readily under mild reaction conditions in contrast to the phenylthio group [21, 22]. Recently, we succeeded in the synthesis of end-functionalized polymer of styrene using diphenyl diselenide in the presence of AIBN at 60°C [23]. We also reported in a previous work [24], that photopolymerization of styrene, in the presence of diphenyl diselenide, produces polystyrene with phenylseleno groups at both chain ends. Furthermore, the resulting polymer underwent the reductive and oxidative elimination of seleno groups produced to polystyrenes with hydrogen and carbon-carbon double bonds at both chain ends, respectively. However, the accurate determination of the structure of the telechelic polymers was very difficult due to the different structures of each chain end in polystyrene. It may interfere with the synthesis of polymer design.

On the other hand, Chu *et al.* [25] reported that the homolysis of the benzylic carbon and the selenium bond, as well as the diselenide bond, occured in the photolysis of dibenzyl diselenide. We examined the photopolymerization of styrene using benzyl phenyl selenide [26]. The end functional polystyrene containing phenyl-seleno group at the ω-chain end of the polymer was obtained (Equation 1). Moreover, this polymer was employed as a prepolymer in the synthesis of the block copolymer (Equation 2).

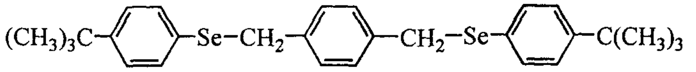


Eq. 1



Eq. 2

As a result, we expected that the photoiniferter containing symmetrical structure would produce a polymer having the same structure at α- and ω-chain ends. In this paper, we describe the preparation of telechelic polystyrene containing seleno groups at both chain ends by novel iniferter, 1,4-bis(*p-tert*-butylphenylselenomethyl) benzene (**XBTSE**), and the conversion of this polymer to other useful symmetrical telechelic polymers.



XBTSE

EXPERIMENTAL

Materials

Styrene was purified by ordinary methods and distilled in a stream of nitrogen just before use. AIBN was recrystallized from methanol. Solvents and other reagents were used after ordinary purification.

Synthesis of 1,4-Bis(*p-tert*-butylphenylselenomethyl) benzene (XBTSE)

Selenium powder (14.8 g, 0.19 gram atom) was added gradually over 30 minutes to a solution of 4-*tert*-butylphenylmagnesiumbromide prepared from magnesium (4.8 g, 0.2 gram atom) and 1-bromo-4-*tert*-butylbenzene (42.0 g, 0.2 mol) in anhydrous ether (80 mL), and stirring was continued for an additional 2 hours. Then, to this reaction mixture, 1,4-bis(chloromethyl) benzene (16.4 g, 0.09 mol) was added slowly, and the mixture was further stirred at room temperature for 2 hours. A solution of ammonium chloride (10.7 g, 0.2 mol) in water (40 mL) was added to the reaction mixture, and the product was extracted with ether and dried over anhydrous sodium sulfate. After evaporation of the solvent, the product was recrystallized with ethanol. The yield was 5.37 g (10.8%). mp. 122°C.

NMR (in $CDCl_3$): $\delta = 1.30$ (s, $2C(CH_3)_3$, 18H), 4.05 (s, 2 CH_2, 4H), 7.10 (s, CC_6H_4C, 4H), and 7.27, 7.37 ppm (q, $2SeC_6H_4$, 8H).

Analysis. Calculated for $C_{28}H_{34}Se_2$: C, 63.63%; H, 6.48%. Found: C, 63.38%; H, 6.55%.

Photopolymerization of Styrene with XBTSE

Polymerizations of styrene in the presence of **XBTSE** were carried out in a sealed glass tube which 15 mm diameter. All polymerizations were carried out by irradiation with a Riko 100 W high-pressure mercury lamp at an 8 cm distance at room temperature. After polymerization for a given time, the content of the tube was poured into a large amount of methanol to isolate the polymer. The resulting polymers (**P-1** series) were purified by reprecipitation, followed by drying in vacuum.

Photopolymerization of Styrene with P-1a as a Polymeric Photoiniferter

A sample of polystyrene (**P-1a**, 0.4 g) containing arylseleno ends group, styrene (6 ml) and benzene (4 ml) was divided equally into two polymerization tubes. The solutions were irradiated with a high-pressure mercury lamp at room temperature. After 5 and 12 hours, the reaction mixture was poured into methanol. The resulting polymers were dried in vacuum.

Reductive Elimination of Seleno Groups in Polystyrene (P-1)

A solution of polystyrene (**P-1b**, 0.2 g), tri-*n*-butyltin hydride (0.19 g) and AIBN (0.8 mg) in benzene (1 mL) was refluxed under nitrogen for 30 hours at 80°. After evaporation of the solvent, the residue was poured into methanol. The resulting polymer (**P-3**) was reprecipitated from THF with methanol, and followed by drying in vacuum. The yield was 0.18 g (90%).

Synthesis of Polystyrene Having Carbon-Carbon Double Bonds at Both Chain Ends

A solution of polystyrene (**P-1c**, 6.1 g), containing arylseleno ends group and 30% aqueous hydrogen peroxide (8.1 g) in THF (60 mL), was stirred for 1 week at room temperature. After evaporation of THF, the residue was poured into methanol to precipitate a polymer. The resulting polymer (**P-4a**) was purified by reprecipitation from THF with methanol, and followed by drying in vacuum. The yield was 5.87 g (96.3%).

Synthesis of Polystyrene Having Epoxy Groups at Both Chain Ends

To a solution of *m*-chloroperbenzoic acid (4.95 g) in methylene chloride (150 mL), polystyrene (**P-4b**, 3.0 g), containing carbon-carbon double bond ends group, was added at 0°C. After the reaction mixture was stirred for 24 hours at 0°C, an aqueous solution of sodium thiosulfate (20 mL) and an aqueous solution of sodium hydrogen carbonate (20 mL) were added, and the reaction mixture was stirred for an additional 1 hour at 0°C. The mixture was extracted with methylene chloride, washed with hydrogen carbonate aqueous solution, and dried with anhydrous sodium sulfate. After evaporation of the solvent, the product was precipitated by a large amount of methanol. The resulting polymer (**P-5**) was reprecipitated from THF with methanol, and followed by drying in vacuum. The yield was 2.87 g (95.0%).

Hydroxylation of β-Methylstyrene as a Model Reaction

To a solution of β-methylstyrene (0.3 g) and THF 10 mL, 1 M borane-tetrahydrofurane complex (10 mL) was added. The reaction mixture was stirred for 1.5 hours at room temperature. Then, a solution of water (2.5 mL), 3 M sodium hydroxide (3.5 mL) and 30% aqueous hydrogen peroxide (3.5 mL) was slowly added. The reaction mixture was further stirred for 1.5 hours at room temperature, extracted with ethyl ether, washed with excess of water, and dried with anhydrous sodium sulfate. After evaporation of the solvent, the product was isolated by column chromatography on silica gel with benzene as developing solvent. The yield was 0.25 g (73%).

NMR (in $CDCl_3$): $\delta = 0.86$ (q; $-CH_3-$), 1.16 (q; $-CH_3-$), 1.72 (t; $-CH_2-$), 2.70 (t; $-CH_2-$), 3.46 (d; -CH-), and 4.56 (d; -CH-).

Synthesis of Polystyrene Having Hydroxyl Groups at Both Chain Ends

To a stirring solution of polystyrene (**P-4c**, 3.0 g) containing carbon-carbon double bond ends group in THF (150 mL), 1 M borane-tetrahydrofurane complex (36 mL) was slowly added. The reaction mixture was stirred for 2 hours at room temperature, and then was stirred for an additional 2 hours at 40°C. A solution of water (37.5 mL), 3 M sodium hydroxide (52.5 mL), and 30 % aqueous hydrogen peroxide (52.5 g) was slowly added, and the mixture was further stirred for 3 hours at room temperature. Then the mixture was extracted with ethyl ether, washed with excess of water, and dried with anhydrous sodium sulfate. After evaporation of the solvent, the product was precipitated by a large amount of methanol. The resulting polymer (**P-6**) was reprecipitated from THF with methanol, and followed by drying in vacuum. The yield was 2.82 g (93.4%).

Synthesis of Polystyrene Having Iodide Groups at Both Chain Ends

To a stirring solution of polystyrene (**P-4d**, 0.2 g) containing carbon-carbon double bond ends group in THF (130 mL), 1 M borane-tetrahydrofurane complex (4.7 mL) was slowly added. The reaction mixture was stirred for 15 hours at room temperature. Then, 1 M methanolic sodium acetate (9.4 mL), 1 M sodium iodide (9.4 mL) and 0.5 M chloramine T (9.4 mL) was added, and further stirred for 1 hour at room temperature. The mixture was quenched by adding aqueous sodium thiosulfate and HCl, and poured into a solution of water (20 mL) and hexane (10 mL). Washing of the hexane layer with water was repeated three times. After evaporation of the solvent, the product was precipitated by a large amount of methanol. The resulting polymer (**P-7**) was reprecipitated from methylene chloride with methanol, and followed by drying in vacuum. The yield was 0.16 g (80%).

Measurements

The number-average molecular weight ($\overline{M}_n$) and weight-average molecular weight ($\overline{M}_w$) were determined by means of gel permeation chromatography (GPC) by polystyrene calibration standards on a Tosoh HLC-803D apparatus. IR spectra were taken with a Nicolet Impact-400D spectrameter. ^{1}H–NMR spectra were recorded by a Jeol JNM–GX400 spectrometer at 400 MHz in $CDCl_3$ with tetramethylsilane (TMS) as an internal reference. Thermo-gravimetric (TG) analysis was performed on a Seiko Denshi TG-DTA 220 instrument in air (flow rate; 200 ml/min) at a heating rate of 10°C/min. Elementary analysis was carried out with Yanaco CHN CORDER MT–3.

RESULTS AND DISCUSSION

In order to obtain the information about the behavior of 1,4-bis(*p-tert*-butylphenylselenomethyl) benzene (**XBTSE**), the polymerization was carried out

TABLE 1. Photopolymerization of Styrene in the Presence of 1,4-bis(*p*-*tert*-butylphenylselenomethyl)benzene (**XBTSE**) using a 100 W high Pressure Hg Lamp at Room Temperature

Run	[XBTSE]/[Styrene] [a]	Time h	Yield [b] %	$\overline{M}_n$ [c] $\times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
1	0	10	2.9	6.60	4.00
2	0.0002	10	8.7	1.81	2.48
3	0.001	10	16.3	0.95	2.17
4	0.002	10	21.3	0.60	2.23
5	0.01	10	21.8	0.34	2.03

[a] Styrene = 5 ml

[b] Recovery of polymer which was insoluble part to methanol.

[c] Estimated by GPC

on irradiation with a high pressure mercury lamp to the solution of styrene and **XBTSE** in a Pyrex tube at room temperature. The results are shown in Table 1. These polymerizations proceeded smoothly with various concentrations of **XBTSE**, as opposed to the polymerization was proceeded scarcely in the absence of **XBTSE**. Moreover, an increase in the amount of **XBTSE** reduced the number average molecular weight ($\overline{M}_n$). The same behavior was shown in the polymerization of styrene with *p*-xylylene bis(N,N-diethyldithiocarbamate) [12] which has large chain transfer constant. Recently, the chain transfer constant of benzyl phenyl selenide for the polymerization of styrene with 2,2'-azobisisobutyronitrile (AIBN) at 60°C has been estimated to be 1.04 [27], which is larger than the value of diphenyl disulfide (0.15). From these results, it was confirmed that **XBTSE** acts as a photoiniferter for the polymerization of styrene.

Figure 1 shows the time-yield and time-average number molecular weight ($\overline{M}_n$) relation in the photopolymerization of styrene with **XBTSE** (0.001 molar equiv. relative to monomer). The polymer yield and $\overline{M}_n$ of the resulting polymers are seen as increasing with the reaction time. Moreover, $\overline{M}_n$ increased with the

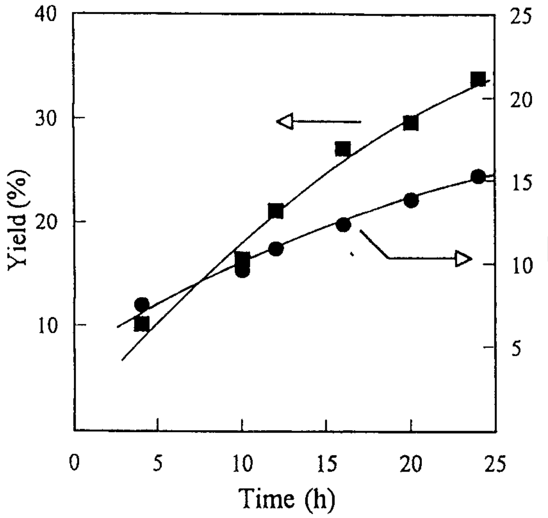


Figure 1. Time-yield (■) and time-$\overline{M}_n$ (●) relations in photopolymerization of styrene with **XBTSE** as a photoiniferter.
[styrene] = 8.7 mol/L, [**XBTSE**]/[styrene] = 0.001

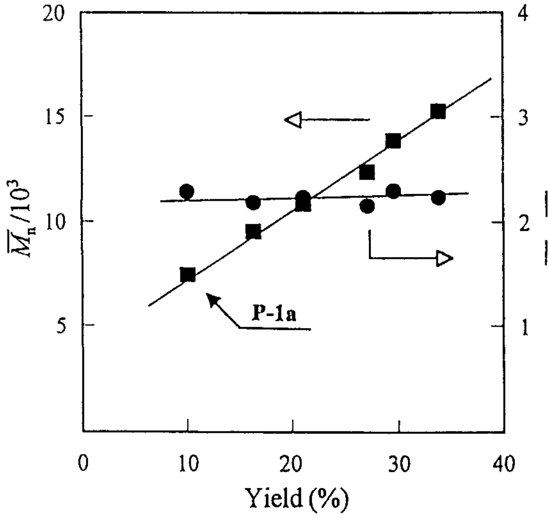
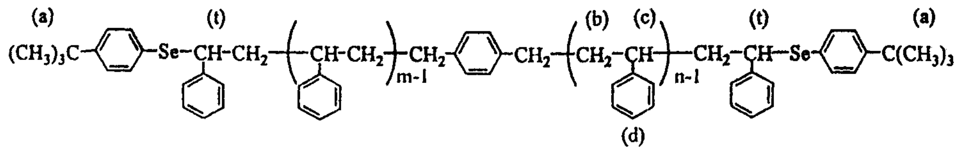


Figure 2. Yield - $\overline{M}_n$ (■) and yield - $\overline{M}_w$/ $\overline{M}_n$ (●) relations for photopolymerization of styrene with **XBTSE** as a photoiniferter.
[styrene] = 8.7 mol/L, [**XBTSE**]/[styrene] = 0.001



P-1a

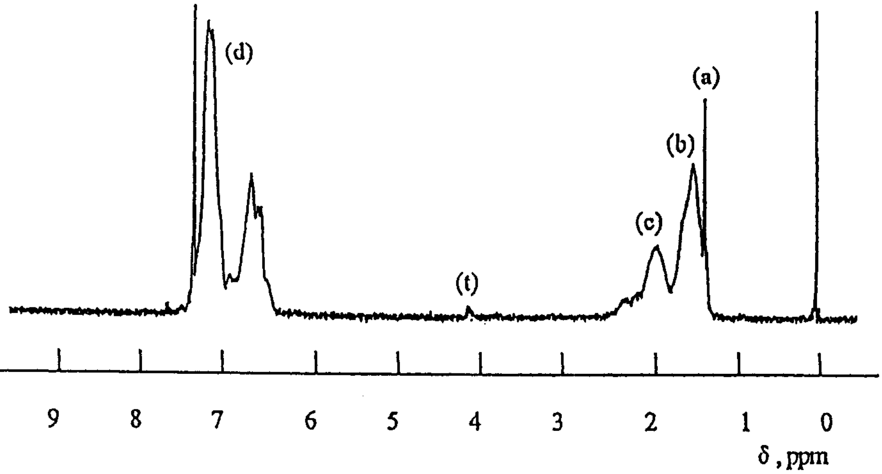


Figure 3. ^{1}H NMR spectrum (400MHz, in CDCl$_3$) of (1) **P-1a** ($\overline{M}_n$=7,400, $\overline{M}_w/\overline{M}_n$=2.27)

polymer yield, as shown in Figure 2. These results indicate that this polymerization shows a living-like nature in limited conversion ranges.

The structure of the chain ends of the resulting polymer (**P-1a**, $\overline{M}_n$=7,400, $\overline{M}_w/\overline{M}_n$ =2.27) in Figure 2 was investigated, and the ^{1}H-NMR spectrum is presented in Figure 3. The signal of *tert*-butyl group can be seen at 1.28 ppm. The singlet signal form of the *tert*-butyl group was revealed by the fact that the structure of both chain ends of the resulting polystyrene is the same. By comparing the average number molecular weight by GPC with the peak intensity ratio of *tert*-butyl signal to phenyl group signals at 6.3-7.4 ppm or to methine signal of polystyrene backbone at 1.6-2.3 ppm, the chain end functionality was calculated to be 1.9.

Next, in order to confirm the structure of arylseleno chain ends, the photopolymerization of styrene with **P-1a** as a starting polymer was carried out for 5 and 12 hours. As seen from Figure 4, $\overline{M}_n$ values of the resulting polymers

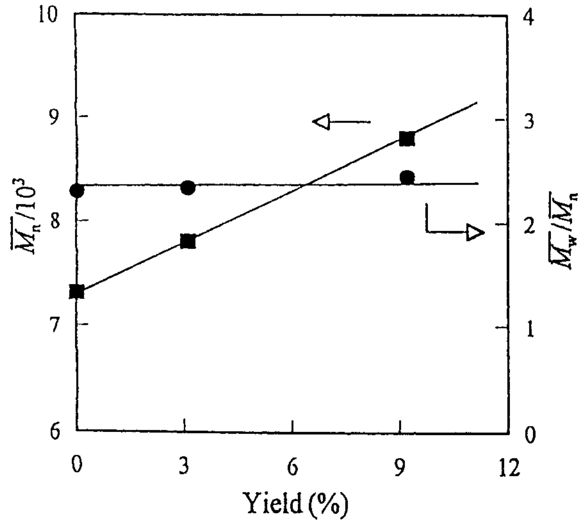
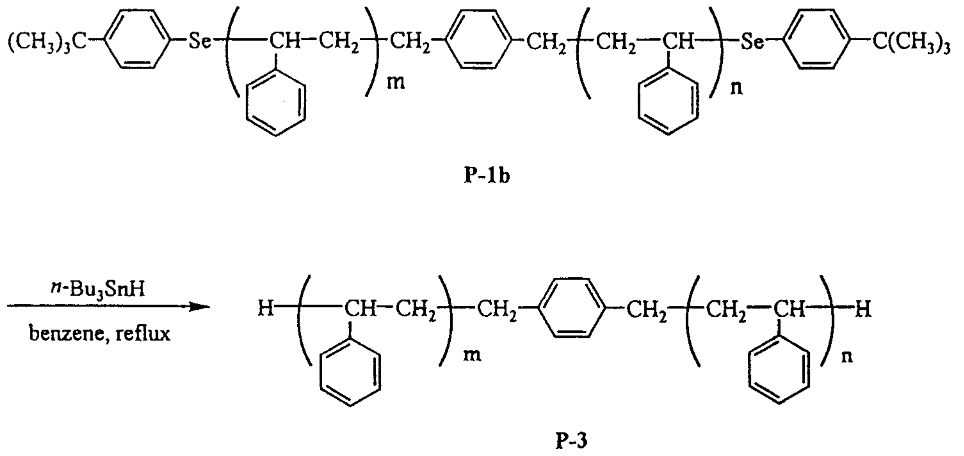


Figure 4. Yield - $\overline{M}_n$ (■) and yield - $\overline{M}_w/\overline{M}_n$ (●) relations for photopolymerization of styrene with **P-1a**.($\overline{M}_n$ =7,400, $\overline{M}_w/\overline{M}_n$= 2.27)

increased with polymer yields. Here, polydispersities were almost unchanged (2.27 ~ 2.44). This result shows that the polystyrene, having seleno groups at both chain ends, effectively worked as a polymeric photoiniferter.

An important characteristic of the phenylseleno group, in contrast to the phenylthio group, is readily removed under mild reaction conditions. According to this fact, the reductive elimination of polystyrene (**P-1b**, $\overline{M}_n$=3,300, $\overline{M}_w/\overline{M}_n$ =1.85) contains arylseleno groups at both chain ends was carried out with tri-*n*-butyltin hydride in the presence of AIBN by refluxing in benzene solution (Equation 3). As can be seen in the ^{1}H-NMR spectrum of the resulting polymer (**P-3**, $\overline{M}_n$=2,900, $\overline{M}_w/\overline{M}_n$ =1.87), the signal of the *tert*-butyl group (δ 1.28 ppm) completely disappeared (Figure 5). Furthermore, the difference of $\overline{M}_n$ between **P-1b** and **P-3** by GPC is very similar to the calculated value (424). Judging from the above facts, the reaction proceeded quantitatively, and polystyrene having hydrogen at both chain ends was successfully prepared.

Figure 6 shows the TG curves of **P-1b** and **P-3**. 1% Weight loss temperatures of **P-1b** and **P-3** are 273°C and 292°C, respectively. It is clear that the thermal stability of polystyrene was improved by the elimination of the seleno groups in both chain ends of the polymer.



Eq. 3

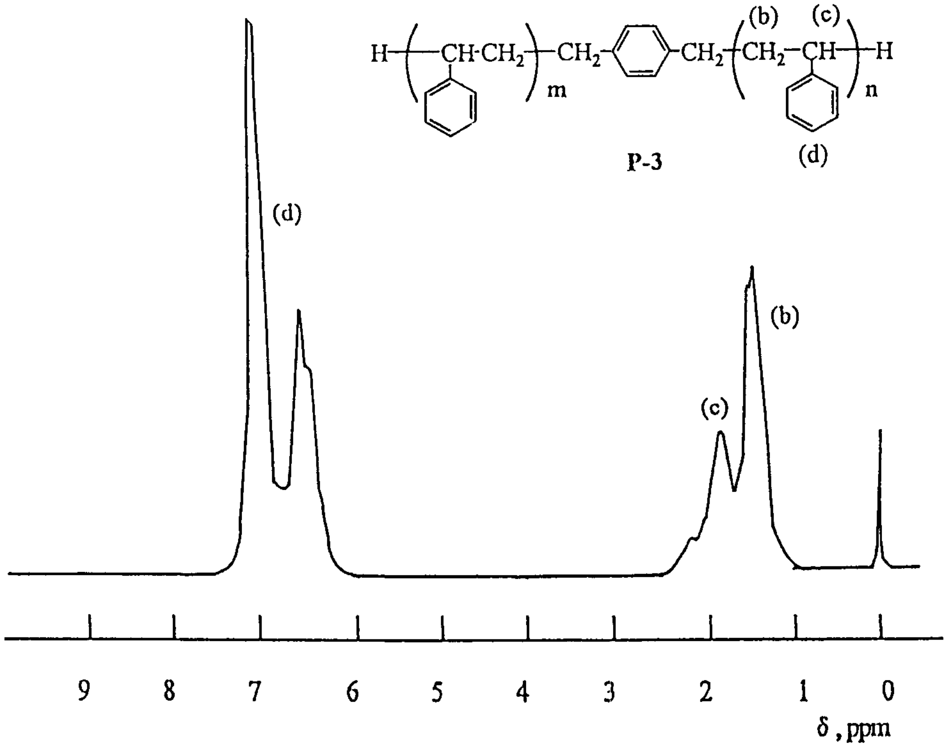


Figure 5. ^{1}H NMR spectrum (400MHz, in $CDCl_3$) of **P-3** ($\overline{M}_n$ =2,900, $\overline{M}_w/\overline{M}_n$= 1.87).

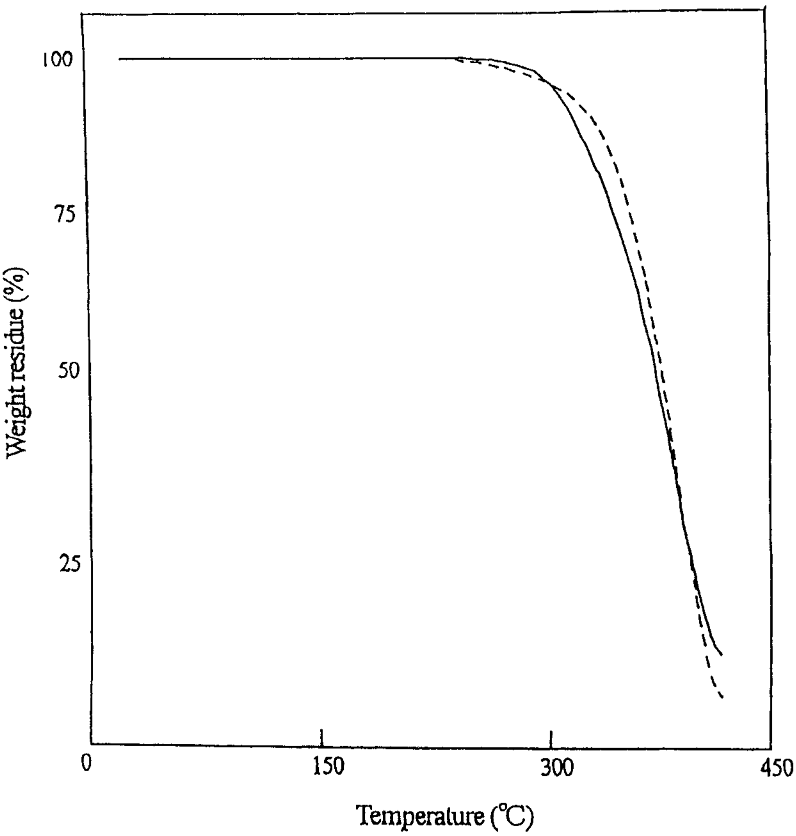
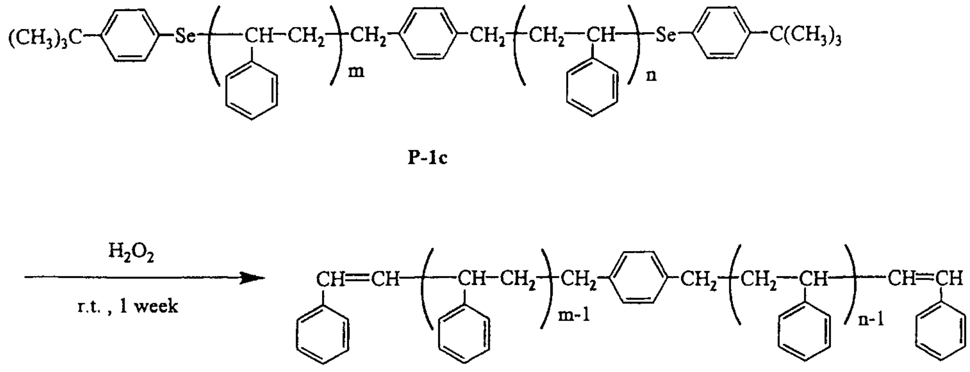


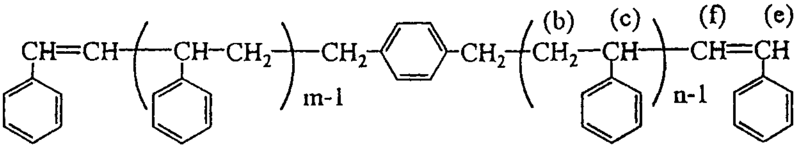
Figure 6. TG curves of **P-1b** (---) and **P-3** (—) at heating rate of 10°C/min. in air.



P-1c

P-4a

Eq. 4



P-4a

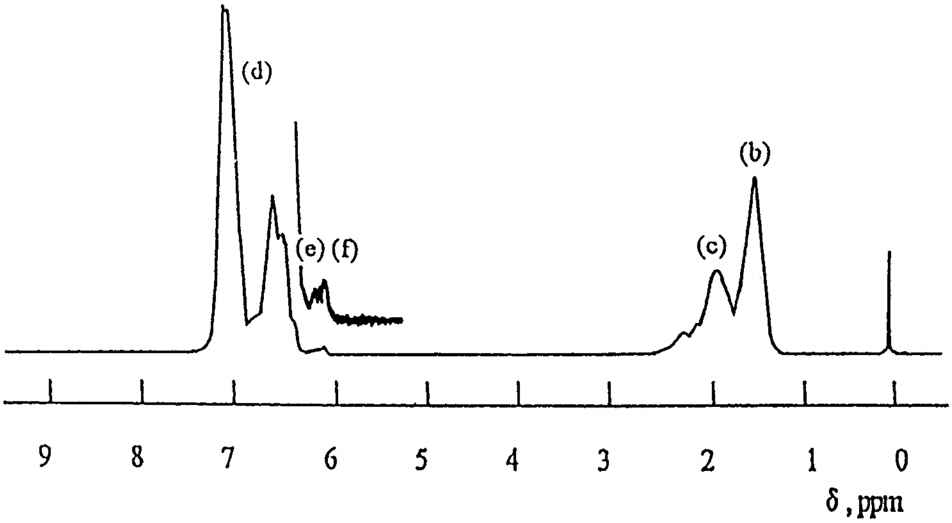
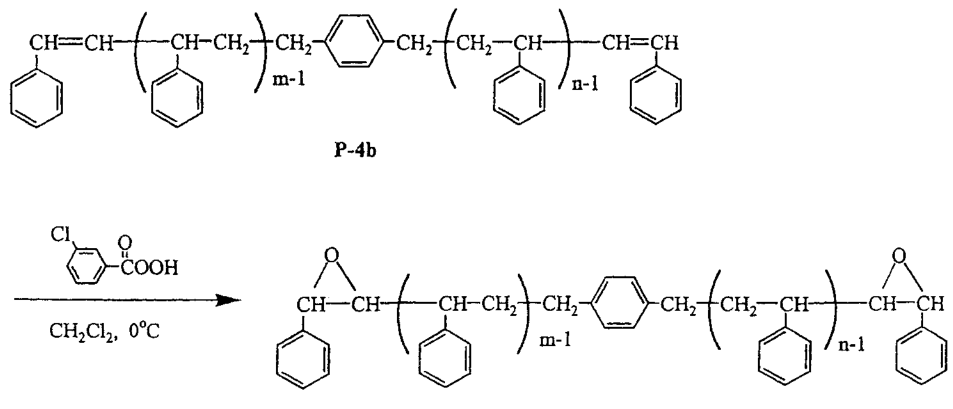


Figure 7. ^{1}H NMR spectrum (400MHz, in $CDCl_3$) of **P-4a** ($\overline{M}_n$ =5,240, $\overline{M}_w/\overline{M}_n$=1.83)

On the other hand, synthesis of polystyrene containing carbon-carbon double bonds at α,ω-chain ends was performed by treatment with hydrogen peroxide for polystyrene (**P-1c**, $\overline{M}_n$=5,700 , $\overline{M}_w/\overline{M}_n$ =1.84) having arylseleno chain ends as shown in Equation 4. The desired polymer, **P-4a**, was obtained at a yield of 97%. As the ^{1}H-NMR spectrum of **P-4a** ($\overline{M}_n$=5,240 , $\overline{M}_w/\overline{M}_n$ =1.83) shows, the signal of the *tert*-butyl group (δ 1.28 ppm) completely disappeared, and the signals, due to the double bond adjacent to the methine group of polystyrene backbone, appeared at around δ 6.0 ppm (Figure 7) .

Carbon-carbon double bonds in the chain end are well known as being very useful for many applications due to the fact that the double bond property is readily modified into other functional groups by various reactions such as hydroboration, hydrosilation, and halogenation [28-30]. First, polystyrene, having an epoxy group at terminal end, was synthesized from polystyrene (**P-4b**,



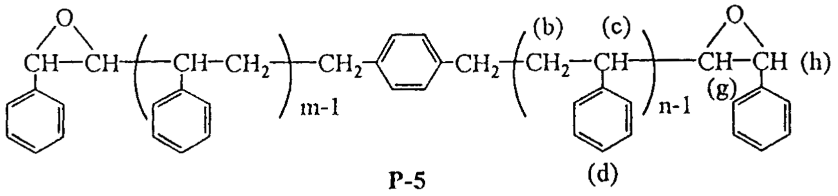
P-4b

P-5

Eq. 5

$\overline{M}_n$=4,000, $\overline{M}_w$/ $\overline{M}_n$=2.05) contains carbon-carbon double bonds at both chain ends by epoxidation with *m*-chloroperbenzoic acid (Equation 5). Figure 8 shows the ^{1}H-NMR spectrum of the resulting polymer (**P-5**, $\overline{M}_n$=4,500, $\overline{M}_w$/ $\overline{M}_n$ =2.00). The signal of the carbon-carbon double bond completely disappeared and new signals assigned to the epoxy group appeared (δ 3.10-3.70 , 4.05 ppm).

Next, **P-4c** ($\overline{M}_n$=5,040, $\overline{M}_w$/ $\overline{M}_n$=1.91) was treated with 1 M borane-tetrahydrofurane complex, followed by 30% aq hydrogen peroxide (Equation 6). Figure 9(a) shows the ^{1}H NMR spectrum of polystyrene (**P-6**, $\overline{M}_n$=5,070, $\overline{M}_w$/ $\overline{M}_n$=1.81), and contains hydroxyl groups at both chain ends. The olefinic double bond signals from **P-4c** also completely disappeared. New signals (δ 3.50, 4.50 ppm), due to a hydroxyl group appeared, and the rate of peak intensities appears to be 1:3. These signals indicated that the chain ends of P-6 have complex structures. It is thought that this results from the effect of Markovnikov's orientation, and it agreed very closely with that obtained by the model experiment with β-methylstyrene as mentioned above. On the other hand, polystyrene (**P-7**, $\overline{M}_n$=4,600, $\overline{M}_w$/ $\overline{M}_n$=1.69) containing iodide groups at both chain ends, was prepared with chloramine-T as an oxidizing agent through hydroboration by borane-tetrahydrofurane complex (Equation 7). Figure 9(b) shows the ^{1}H NMR spectrum of **P-7**. The signals of the double bond due to **P-4d** ($\overline{M}_n$=4,130, $\overline{M}_w$/ $\overline{M}_n$=1.80) disappeared. From the appearance of new signals (δ 3.50, 4.55 ppm), we confirmed that polystyrene, having an iodide group at both chain ends, was successfully prepared.



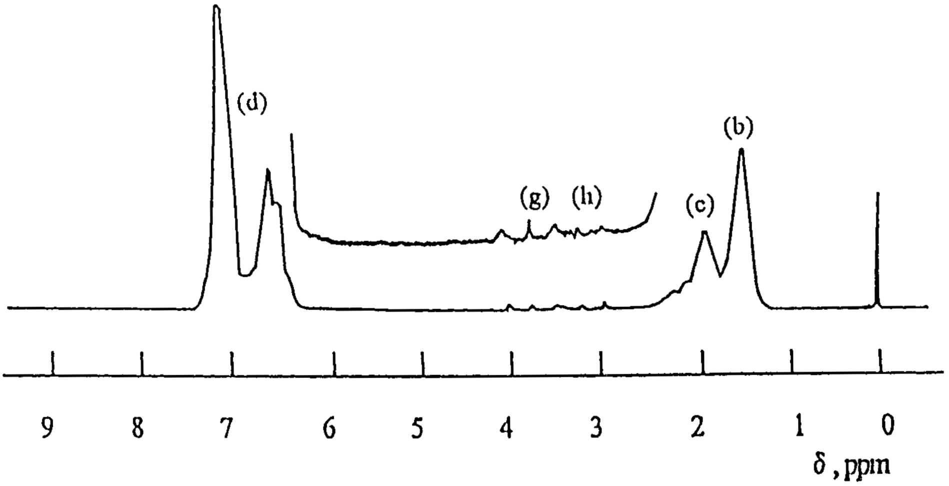
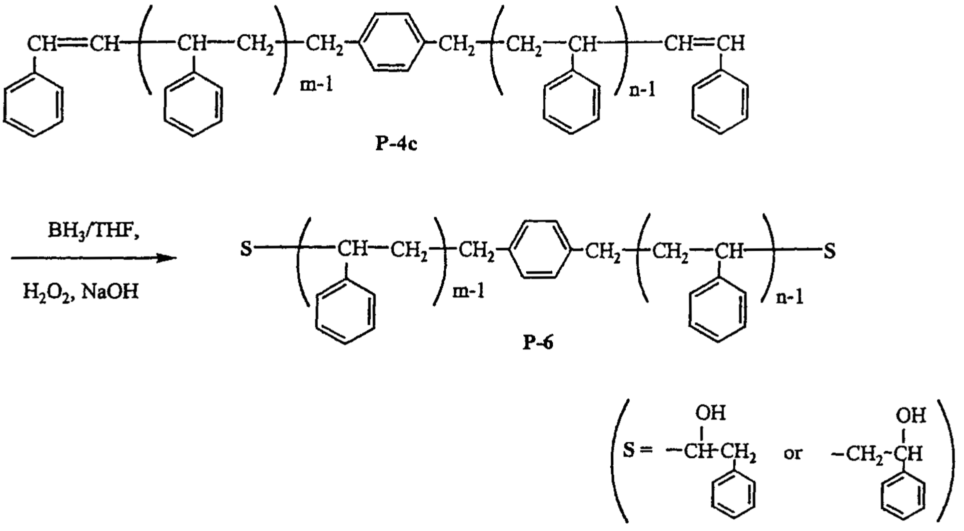


Figure 8. ^{1}H NMR spectrum (400MHz, in CDCl$_3$) of **P-5** ($\overline{M}_n$ =4,500, $\overline{M}_w/\overline{M}_n$=2.00)



Eq. 6

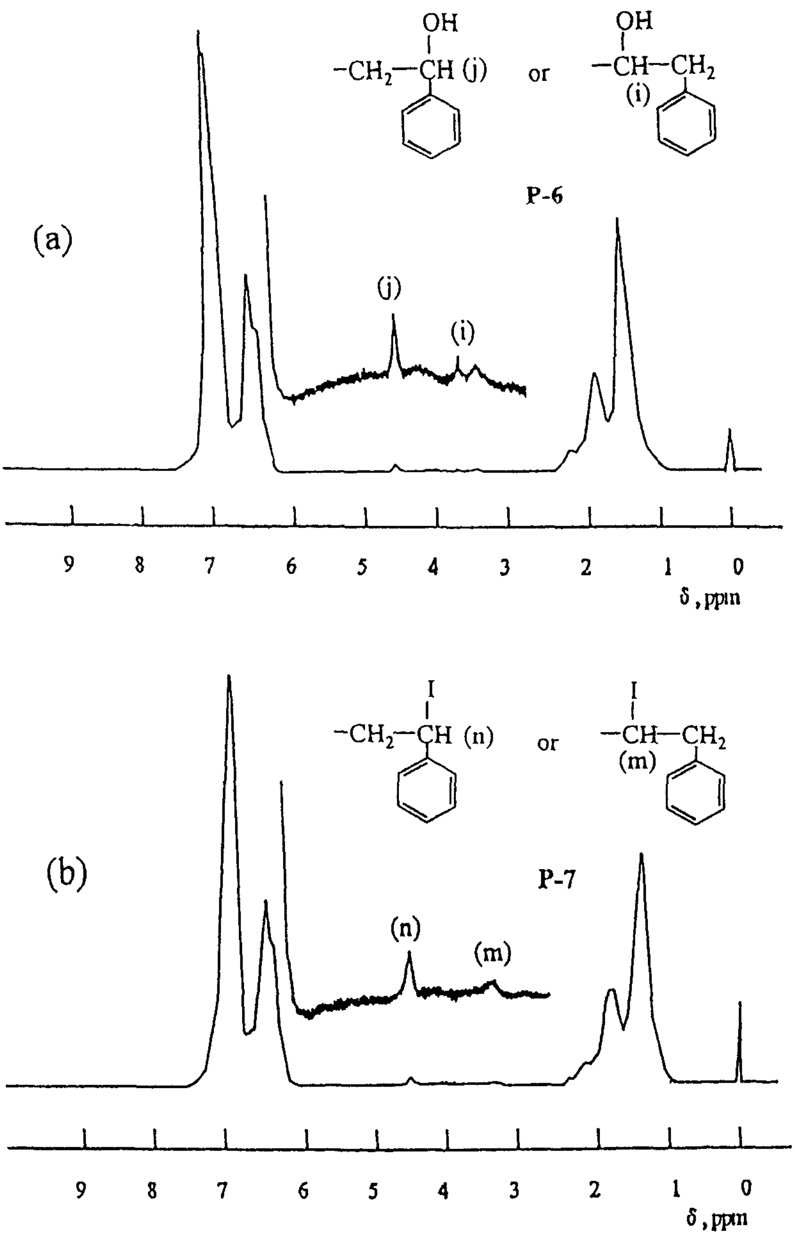
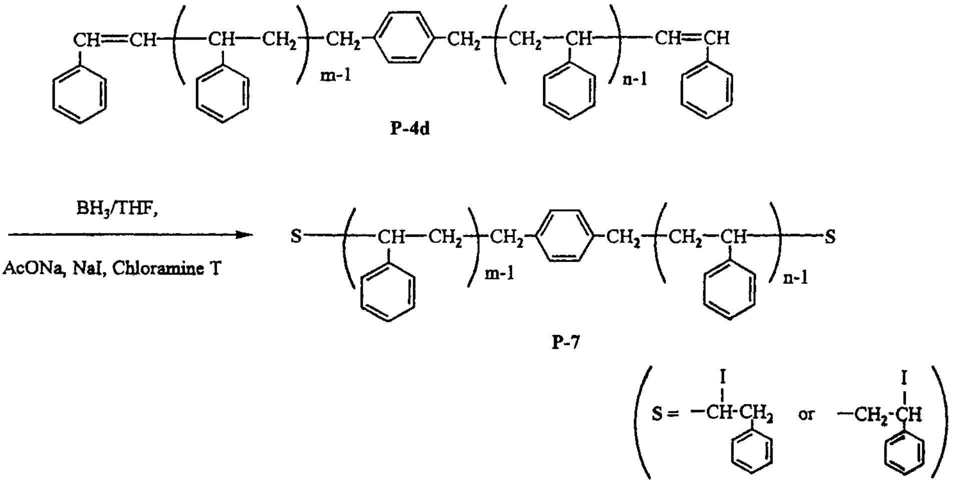


Figure 9. ^{1}H NMR spectrum (400MHz, in $CDCl_3$) of (a) **P-6** ($\overline{M}_n = 5{,}070$, $\overline{M}_w/\overline{M}_n = 1.81$) and (b) **P-7** ($\overline{M}_n = 4{,}600$, $\overline{M}_w/\overline{M}_n = 1.69$)



Eq. 7

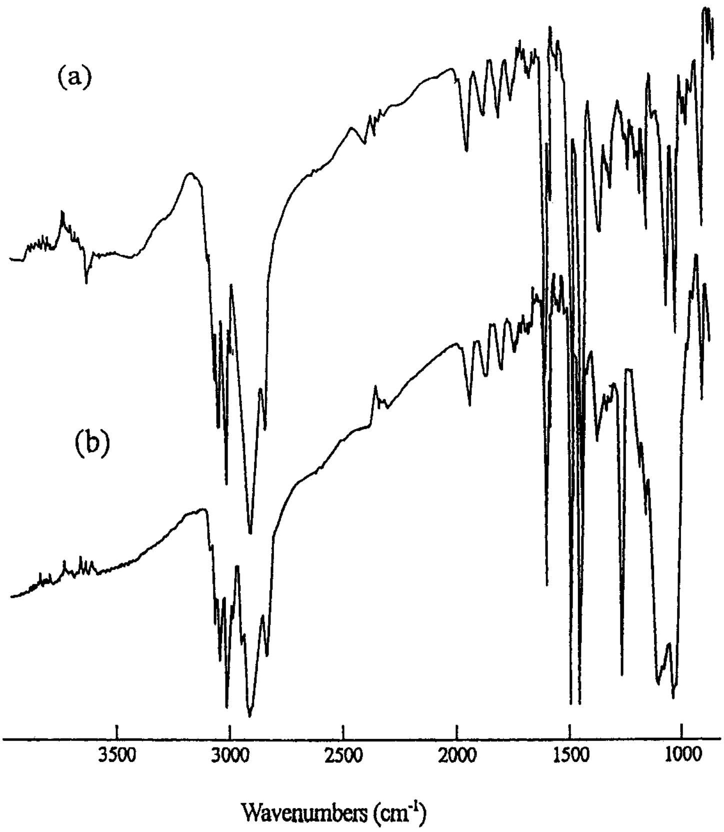


Figure 10. IR spectra of (a) **P-6** ($\overline{M}_n$ = 5,070, $\overline{M}_w/\overline{M}_n$=1.81) and (b) **P-7** ($\overline{M}_n$ = 4,600, $\overline{M}_w/\overline{M}_n$=1.69)

Furthermore, **P-6** and **P-7** were also confirmed by IR spectra (Figure 10), which shows characteristic absorption of the hydroxyl group at about 3369 cm^{-1} for **P-6**.

From the above results, the polystyrene containing seleno groups at both chain ends was converted quantitatively to other useful symmetrical telechelic polystyrenes with suitable agents.

CONCLUSION

1,4-Bis(*p-tert*-butylphenylselenomethyl) benzene **(XBTSE)** functions as a bifunctional photoiniferter for the polymerization of styrene. This polymerization of styrene produced telechelic polystyrene containing arylseleno groups at both chain ends. The thermal stability of polystyrene was improved by the reductive elimination of seleno group at both chain ends in the polymer. In addition, polystyrene, having carbon-carbon double bond at chain ends, was converted to telechelic polystyrenes carrying symmetric terminal groups such as epoxy, hydroxyl, and iodide group, respectively.

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