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

Living Radical Polymerization of Styrene with Diphenyl Diselenide as a Photoiniferter. Synthesis of Polystyrene with Carbon-Carbon Double Bonds at Both Chain Ends

Tae Seok Kwon[a]; Sadanori Kumazawa[a]; Tetsuya Yokoi[a]; Shuji Kondo[a]; Hideo Kunisada[a]; Yasuo Yuki[a]
[a] Department of Materials Science and Engineering, Nagoya Institute of Technology, Showa-ku, Nagoya, Japan

To cite this Article Kwon, Tae Seok , Kumazawa, Sadanori , Yokoi, Tetsuya , Kondo, Shuji , Kunisada, Hideo and Yuki, Yasuo(1997) 'Living Radical Polymerization of Styrene with Diphenyl Diselenide as a Photoiniferter. Synthesis of Polystyrene with Carbon-Carbon Double Bonds at Both Chain Ends', Journal of Macromolecular Science, Part A, 34: 9, 1553 — 1567

To link to this Article: DOI: 10.1080/10601329708010026

URL: http://dx.doi.org/10.1080/10601329708010026

J.M.S.—PURE APPL. CHEM., A34(9), pp. 1553–1567 (1997)

LIVING RADICAL POLYMERIZATION OF STYRENE WITH DIPHENYL DISELENIDE AS A PHOTOINIFERTER. SYNTHESIS OF POLYSTYRENE WITH CARBON-CARBON DOUBLE BONDS AT BOTH CHAIN ENDS

Tae Seok Kwon, Sadanori Kumazawa, Tetsuya Yokoi,
Shuji Kondo*, Hideo Kunisada, and Yasuo Yuki
Department of Materials Science and Engineering
Nagoya Institute of Technology
Gokiso-cho, Showa-ku
Nagoya 466 Japan

ABSTRACT

Photopolymerization of styrene in the presence of diphenyl diselenide proceeded smoothly. The polymer yields and the number average molecular weight (*M*n) of the polymers increased with reaction time. Further, a linear relationship was found for a plot of *M*n for polystyrene versus polymer yield. These results indicate that this polymerization proceeds through a living radical mechanism. Photopolymerization of styrene with bis(*p*-*tert*-butylphenyl) diselenide afforded a telechelic polystyrene with terminal arylseleno groups. The resulting polymer underwent the reductive elimination of terminal seleno groups by the reaction with tri-*n*-butyltin hydride. Moreover, this telechelic polymer was treated with hydrogen peroxide to afford polystyrene with carbon-carbon double bonds at both chain ends.

INTRODUCTION

Living radical polymerization has received much attention in the design and construction of macromolecules. Recently, several new methodologies have been developed remarkably [1-37]. Among them, the iniferter method discovered by Otsu *et al.* [1-4] is attractive for preparing simple block copolymers and more complex polymer architectures by using various monomers which do not polymererize via an ionic mechanism.

They mainly employed organic sulfur compounds such as disulfides and dithiocarbamates as photoiniferters [1, 2]. Since these compounds not only serve as free radical initiators but also have high reactivity for chain transfer and primary radical termination, the polymers formed are end-capped with iniferter fragments. The polymer with sulfide moieties at terminal group also have an initiation ability, and thus by irradiation of the light in vinyl monomers, polymers with increased molecular weight are obtained. Primarily, their success would be believed due to exploiting the characteristic of thiyl radical produced from organic sulfur compounds, because its reactivity to initiation of radical polymerization is very low.

On the other hand, it has been found recently that the phenylseleno radical derived from photolysis of diphenyl diselenide (**1**) or alkyl phenyl selenides is very stable [38-40], and the reactivity towards carbon-carbon double bonds is lower than that of the corresponding sulfur radical, phenylthio radical by a factor of about 10-50. Further, Russel and Tashtoush [41] have reported that diphenyl diselenide undergoes the bimolecular homolytic displacement (SH2) reaction by an alkyl radical about 160 fold faster than diphenyl disulfide. In fact, large chain transfer constant of diphenyl diselenide (28.1) has been estimated for the polymerization of styrene with AIBN at 60°C [42]. It is well known that organic selenium compounds displays unique chemical behavior, especially the removal of phenylseleno group occurs readily under mild reaction conditions in contrast to phenylthio group [43-45].

From these facts, we hoped that diphenyl diselenide would work as a photoiniferter, and the resulting telechelic polymer with phenylseleno groups would be converted to various other useful telechelic polymers. In this paper, we describe the photopolymerization of styrene with a new iniferter via a living radical mechanism, and a facile synthesis of polystyrene with carbon-carbon double bonds at both chain ends.

EXPERIMENTAL

Materials

Styrene was purified by the ordinary method and distilled in a stream of nitrogen just before use. Solvents were purified by distillation after appropriate

$$R{-}R' + nM \longrightarrow R{-}\!\left(M\right)_n\!{-}R' \qquad (1)$$

R—R' : Iniferter
M : Monomer

drying Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol. Diphenyl diselenide (**1**) (λ_{max} = 330 nm, ε =1,270 in ethanol) was prepared according to the literature [46]. Other reagents were obtained commercially and were used without further purification.

Synthesis of Bis(*p*-*tert*-butylphenyl) Diselenide (2)

Selenium powder (7.4 g, 0.94 gram atom) was added gradually over 30 minutes to a solution of *p*-*tert*-butylphenylmagnesium bromide prepared from magnesium (2.4 g, 0.1 gram atom) and 1-bromo-4-*tert*-butylbenzene (21.3 g, 0.1 mol) in anhydrous ether (30 mL). Stirring was continued for an additional 30 minutes. Then, to this reaction mixture, bromine (5.8 g, 0.04 mol) was added slowly with cooling, and further stirred at room temperature for 1 hour. A solution of ammonium chloride (5.3 g, 0.1 mol) in water (15 mL) was added to the reaction mixture, extracted with ether and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a yellow solid. This solid was recrystallized with ethanol. The yield was 3.6 g (18%). mp 70°C.

IR (KBr): 2955, 1594, 1496, 1398, 1362, 1269, 1114, 1010, 814, 726, and 540 cm^{-1}.

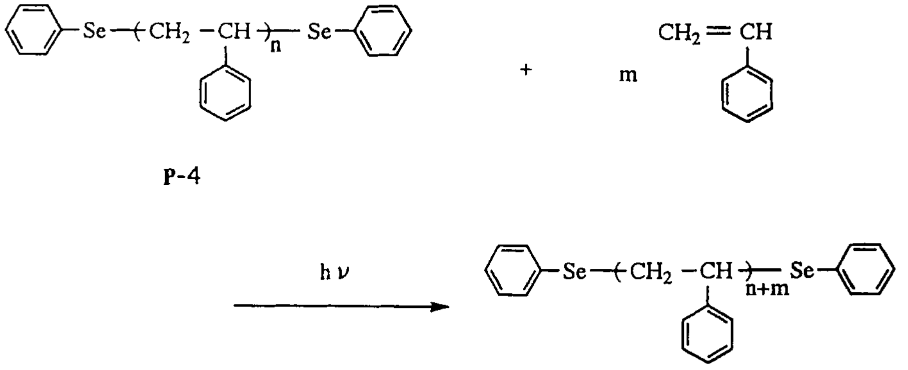
NMR(in $CDCl_3$): δ = 1,30 (s, 18H) and 7,42 ppm (m, 4H).

UV (ethanol): λ_{max} = 335, (ε = 1,330).

Analysis. Calculated for $C_{20}H_{26}Se_2$: C, 56.61; H, 6.18 %. Found: C, 56.45 H, 6.40%.

Photopolymerization of Styrene with Diaryl Diselenides

The required amounts of styrene and diselenide 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 vaccum. 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 a given time, the tube was opened and its contents were poured into a large amount of methanol to precipitate the polymer. The resulting polymer was then purified by reprecipitation, followed by drying in vacuum.



P-4

P-7

(2)

Photopoloymerization of Styrene with P-4

A solution of **P-4** (0.24 g), styrene (3 mL) in benzene (2 mL) was immersed in a Pyrex tube. The tube was degassed under vaccum by the conventional freeze and thaw technique, and sealed off under vacuum. The solution was irradiated with a 100 W high pressure mercury lamp for 10 hours. The tube was opened and the content were poured into methanol. The precipitated polymer (**P-7**) was reprecipitated from methylene chloride to methanol. The yield was 0.48 g.

Synthesis of P-8 by Reductive Elimination of P-6

A solution of **P-6** (0.30 g), tri-*n*-butyltin hydride (0.16 mg), AIBN (0.2 mg) in benzene (5 mL) was refluxed under nitrogen for 8 hours. After evaporation of the solvent, the residue was poured into methanol. The resulting polymer was reprecipitated from methylene chloride with methanol, and followed by drying in vacuum. The yield was 0.23 g (96 %).

Synthesis of P-9 by Oxidative Elimination of P-6

A solution of **P-6** (0.15 g), 30% aq hydrogen peroxide (0.2 g) in THF (3 mL) was stirred for 20 hours at room temperature. After evaporation of most of THF, the residue was poured into methanol to precipitate polymer. The polymer was purified by reprecipitation from methylene chloride with methanol, and followed by drying in vacuum. The yield was 0.12 g (97 %).

Measurements

IR spectra were measured by a Nicolet Impact-400D. NMR spectra were recorded by a Varian XL-200 spectrometer with $CDCl_3$ as solvent using tetra-

TABLE 1. Photopolymerization of Styrene with Diaryl Diselenides[a]

Run	Diselenide	[Diselenide]/ [Styrene]	Time h	Yield[b] %	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$	Polymer
1	None	0	10	2.9	66,000	4.01	**P-1**
2	**1**	0.0025	10	14.5	5,700	2.13	**P-2**
3	**1**	0.005	10	18.4	3,200	1.93	**P-3**
4	**1**	0.01	10	18.3	1,700	1.81	**P-4**
5	**1**	0.015	10	7.2	1,100	1.44	**P-5**
6	**2**	0.01	5	4.2	2,200	2.26	**P-6**

methysilane as the internal standard. UV spectra were measured by a JASCO Ubest-35 spectrometer. Gel permeation chromatography was carried out on a TOSOH HLC-803D with G2000, G3000,and GMH TSK gel-columns and a differential refractometric detector in tetrahydrofuran. The molecular weights were determined using polystyrene standards.

RESULTS AND DISCUSSION

Polymerization of styrene was carried out by irradiation with a high pressure mercury lamp to the solution of styrene and diphenyl diselenide (**1**) (λ_{max} = 330 nm) in a Pyrex glass tube at room temperature. First, in order to obtain the information about the initiation ability of **1**, the polymerization was examined under several initiator concentrations without solvent for 10 hours. The results are shown in Table 1.

The polymerization proceeded smoothly in the presence of **1**, but scarcely afforded polystyrene without **1**. The number average molecular weight $\overline{Mn}$ decreased with the increasing of the amount of **1**. Further, the polymer yield increased when the ratio of **1** to styrene increased from 0 to approximately 0.005, and above this value the polymer yield decreased. A similar finding has been reported for tetraethylthiuram disulfide having large chain tranfer constant [47]. In addition, the polydispersities ($\overline{Mw}/\overline{Mn}$) decreased with increasing the ratio of diphenyl diselenide to styrene. These obsevations strongly indicate that **1** not only serves as a photoinitiator but also works as an effective chain transfer agent. Bis(*p*-*tert*-butyphenyl) diselenide (**2**) (λ_{max} = 335 nm) also displayed photoinitiation ability for polymerization of styrene.

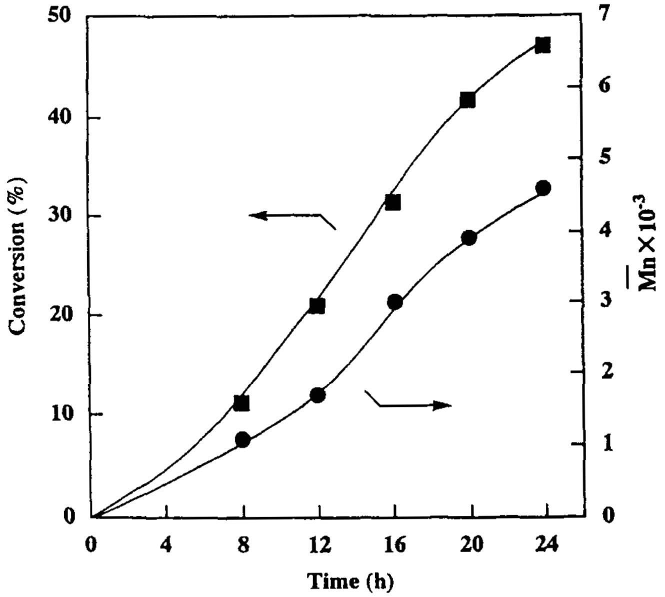


Figure 1. Time - conversion and time - $\overline{Mn}$ relations for photopolymerization of styrene with **1**. [Styrene] = 8.7 mol/L, [**1**] = 0.087 mol/L.

In the photopolymerization of styrene with **1**, the relationship for time-conversion and time- $\overline{Mn}$ of the polymers are shown in Figure 1. From this figure, the polymer yields and $\overline{Mn}$ values of the resulting polymers were found to increase with the reaction time. An almost linear relationship was found for a plot of $\overline{Mn}$ for polystyrene versus polymer yield (Figure 2). Furthermore, $\overline{Mn}$ at 40% conversion is 3,900 ($[M]_0/[I]_0 = 100$). This value is very close to the theoretical value (4,000) for living radical polymerization.

From the above results, it is clear that this polymerization proceeds through a living radical mechanism as expected. However, the polydispersities ($\overline{Mw}/\overline{Mn}$) are 1.6-2.1, which are similar to the values obtained from the living radical polymerization with sulfur compounds by Otsu *et al.* [1].

In order to confirm the living nature of the system, the chain extention experiment was investigated by using the polystyrene, **P-4**. When a solution of **P-4** in styrene was irradiated for 10 hours, the polystyrene, **P-7** was produced.

As shown in Figure 3, the peak in GPC for **P-7** shifted to the higher molecular weight region ($\overline{Mn}$ = 4,200) in comparison with the starting polymer, **P-4** ($\overline{Mn}$ = 1,700). Further, from the weight of the resulting polymer and $\overline{Mn}$, it was

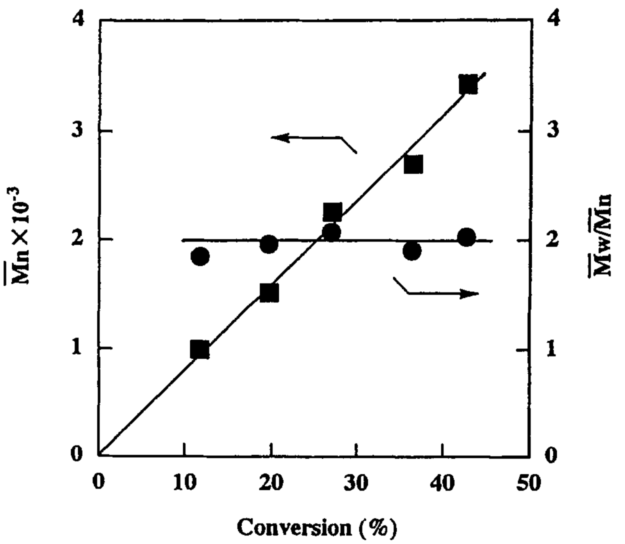


Figure 2. $\overline{Mn}$ - conversion and $\overline{Mw}/\overline{Mn}$ - conversion relations for photopolymerization of styrene with **1**. [Styrene] = 8.7 mol/L, [**1**] = 0.087 mol/L.

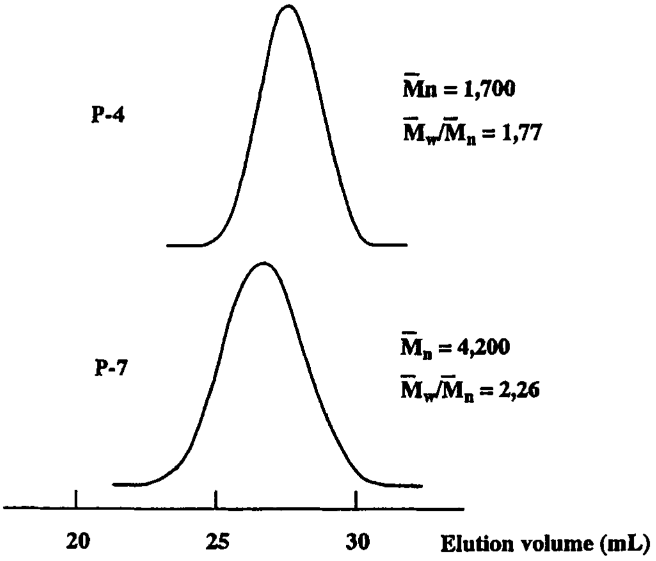
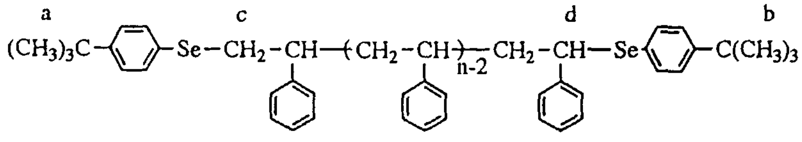


Figure 3. GPC traces of P-4 and P-7.



P-6

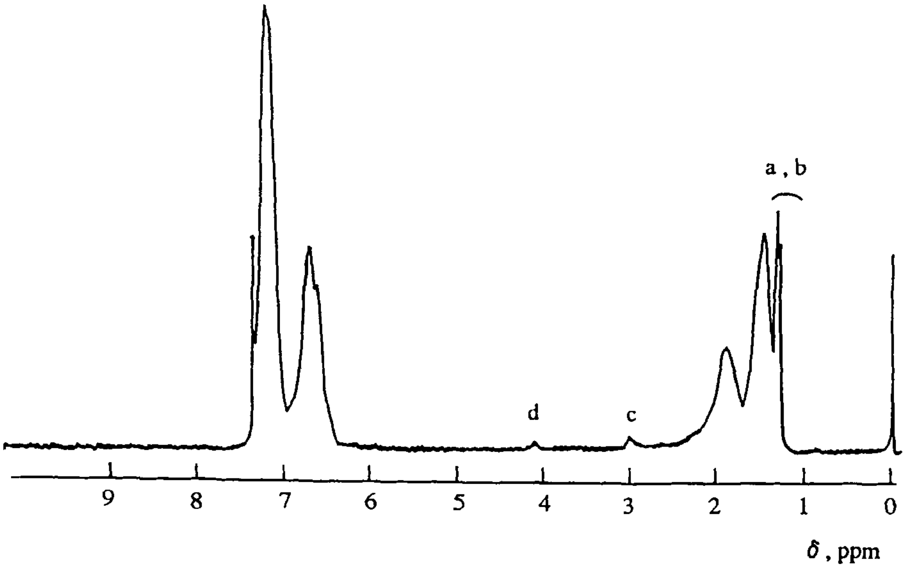


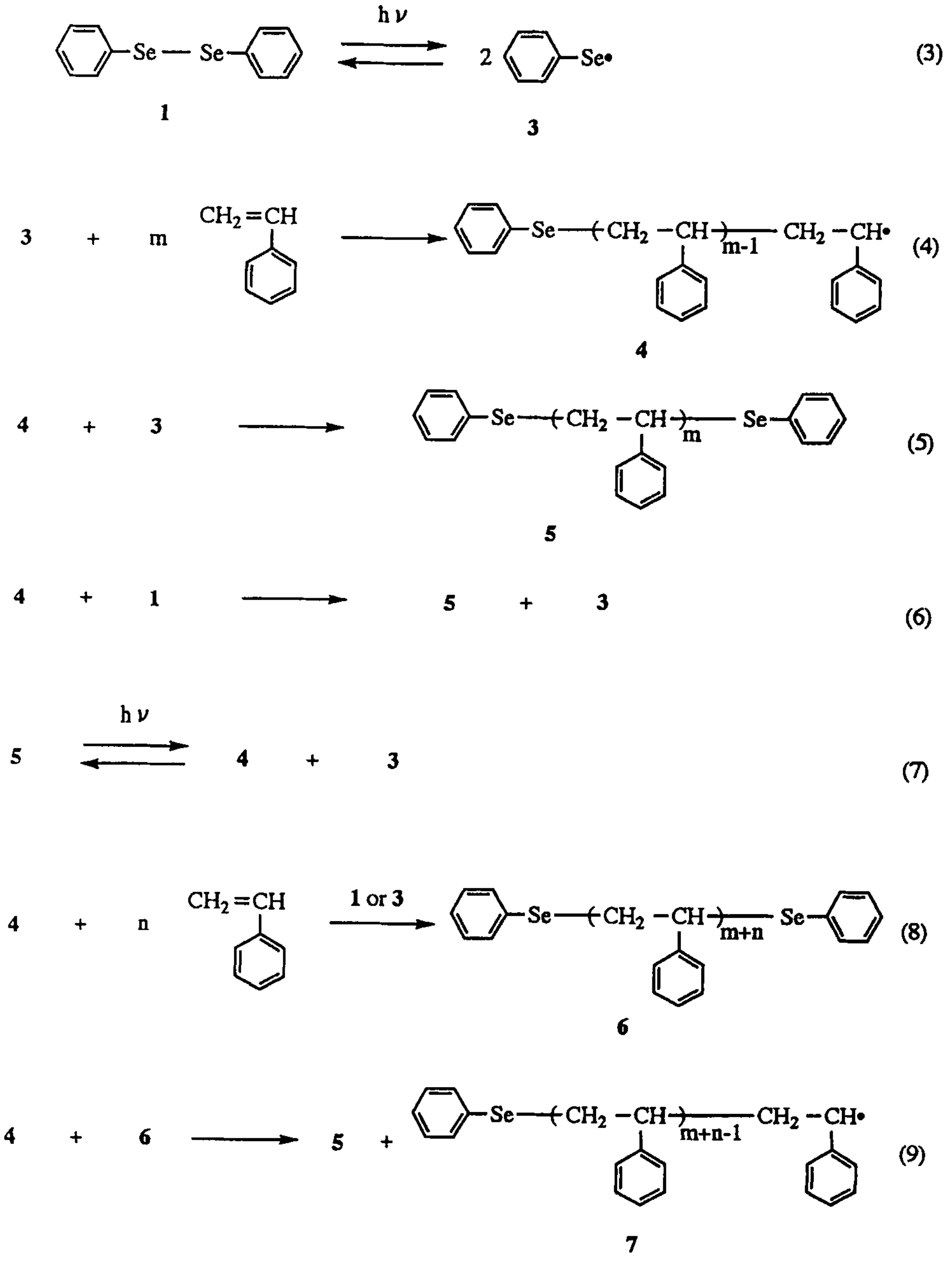
Figure 4. ^{1}H-NMR spectrum of **P-6** (200 MHz, in $CDCl_3$).

found that the number of polymer molecule through the polymerization reaction almost unchanged.

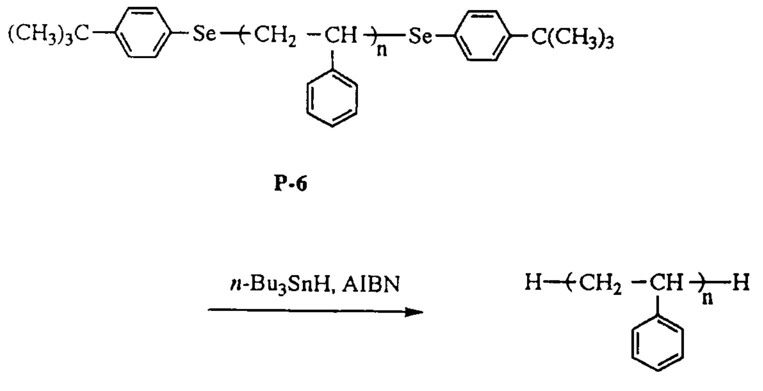
Next, the end group of the resulting polystyrene was investigated by employ-ing **P-6** which was prepared with **2** as a photoiniferter. NMR spectrum of **P-6** is shown in Figure 4. The signals of *tert*-butyl group can be seen at 1.28 and 1.30 ppm. From the ratio of peak intensity of *tert*-butyl group to phenyl group at 6.3-7.4 ppm, the functionality with seleno group was calculated to be 1.9.

From above results, photopolymerization of styrene with **1** is expected to proceed as follows (Scheme 1).

As can be suggested by Ogawa *et al.* [38], **1** would homolytically dissociate to phenylseleno radical (**3**) by photoirradiation (Equation 3). The initiation of polymerization would occur by the addition of **3** to styrene although the rate is very slow (Equation 4). And the propagation would take place by the addition of the


hν
Se — Se
2 Se•
1
3
(3)
3 + m CH2=CH
Se—(CH2 –CH)m-1 CH2 –CH•
4
(4)
4 + 3
Se—(CH2 –CH)m Se
5
(5)
4 + 1 → 5 + 3
(6)
hν
5 ⇌ 4 + 3
(7)
4 + n CH2=CH
1 or 3
Se—(CH2 –CH)m+n Se
6
(8)
4 + 6 → 5 +
Se—(CH2 –CH)m+n-1 CH2 –CH•
7
(9)

Scheme 1



P-6

P-8

(10)

resulting carbon radical to styrene. This polymerization would be terminated by two mechanisms. One is the coupling of polymer radical (**4**) with stable seleno radical (Equation 5) and the other is the effective chain transfer reaction to **1** (Equation 6), that is, SH2 reaction. Further, photoirradiation of the resulting polymer having phenylseleno groups at both chain ends (**5**) leads the cleavage of weak benzylic carbon and selenium bond at ω-terminal preferentially to afford less reactive phenylseleno radical (**3**) and reactive polymeric carbon radical (**4**) towards carbon-carbon double bond (Equation 7). However, the photocleavage of sp^3 carbon and selenium bond at α-terminal cannot be neglected completely because even an alkyl selenide as model compound of α-terminal group have been found to dissociate on UV irradiation [48]. Then, the polymer radical (**4**) adds to styrene, and phenylseleno radical (**3**) mainly participate to the coupling reaction to afford polystyrene with phenylseleno groups (Equation 8). Here, the coupling reaction of polystyryl radicals (**4**) can be neglected because terminal structure of polystyrene, **P-6** is not the same. Therefore, these are essentially the same mechanisms proposed by Otsu *et al.* [1,2] for tetraethylthiuram disulfide as an iniferter. However, in this living polymerization mechanism, the attack of growing polymer radical (**4**) to the selenide moiety at other polymer chain end (Equation 9) would not be excluded, because selenium atom in selenide is known to undergo the attack of free radical to afford carbon radical [49].

The synthetic utility of telechelic polystyrene having phenylseleno groups was demonstrated by two reactions which are well-known for organic selenium compounds [50, 51]. Initially, reductive elimination of **P-6** with tri-*n*-butyltin hydride in the presence of AIBN was examined. The reaction was carried out by refluxing the reaction mixture in benzene under nitrogen.

The NMR spectrum of the resulting polymer, **P-8** ($\overline{Mn}$,=1,800, $\overline{Mw}/\overline{Mn}$, = 2,14) showed that the *p-tert*-butylphenylseleno group was completely converted to

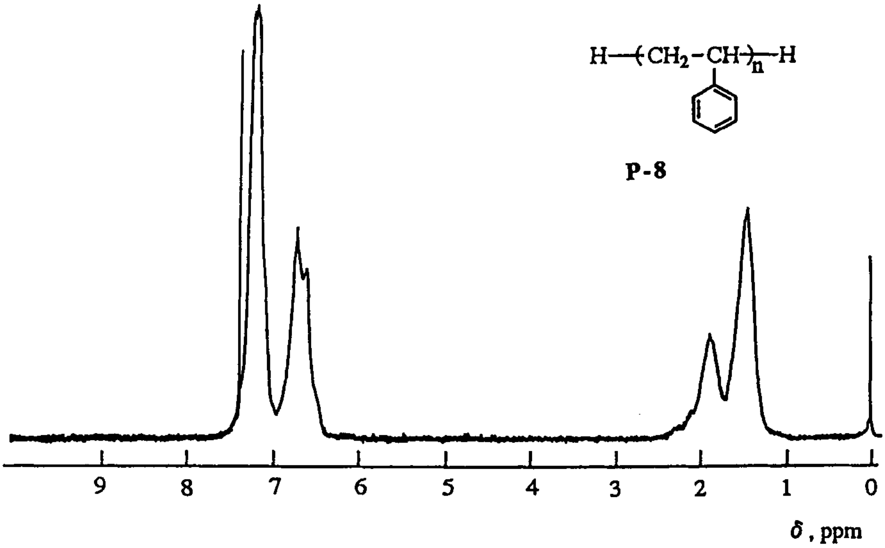
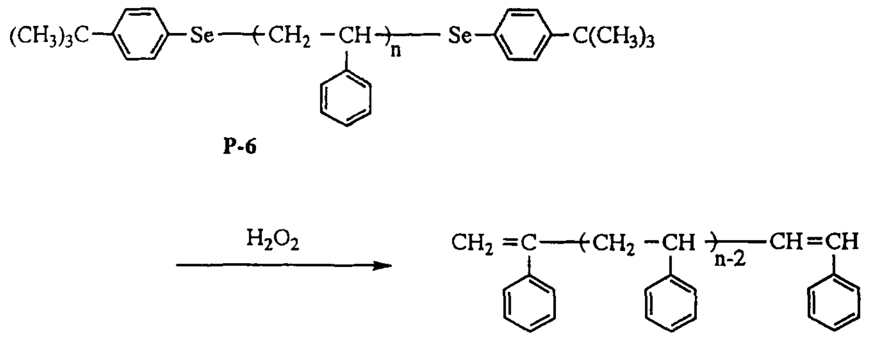


Figure 5. ^{1}H-NMR spectrum of **P-8** (200 MHz, in $CDCl_3$).

hydrogen (Figure 5). This reaction is important because stability of the polymer would be increased significantly due to the elimination of reactive seleno groups. Further, this polystyrene is of interest, in view of the structure, because both terminal groups are hydrogens.

Next, elimination of selenoxide as the most useful reaction of organic seleno compounds in synthetic chemistry, was applied to the above polymer [49]. When a solution of telechelic polystyrene, **P-6** in THF was treated with 30% aq hydrogen peroxide at room temperature, the polymer, **P-9** ($\overline{Mn}$, =1,800, $\overline{Mw}/\overline{Mn}$, = 2.06) was obtained in 97% yield. The NMR spectrum of this polymer is shown in Figure 6. From the NMR spectrum of the resulting polymer, the signals of *tert*-butyl group disappeared and revealed the signals of vinyl protons at 4.75 and 5.07 ppm and vinylene protons at 6.03-6.20 ppm. Further, the difference of $\overline{Mn}$, between **P-6** and **P-9** is very similar to twice the molecular weight of *tert*-butylphenylselenol (2 x 213). Therefore, it is obvious that the polymer was oxidized to the corresponding polymer with terminal selenoxide, and followed by the elimination to give a polymer containing different double bonds at terminal groups. Moreover, the appearance of two kind of double bonds supports the structure of the polystyrene, **P-6** with terminal seleno groups.



P-6

P-9

(11)

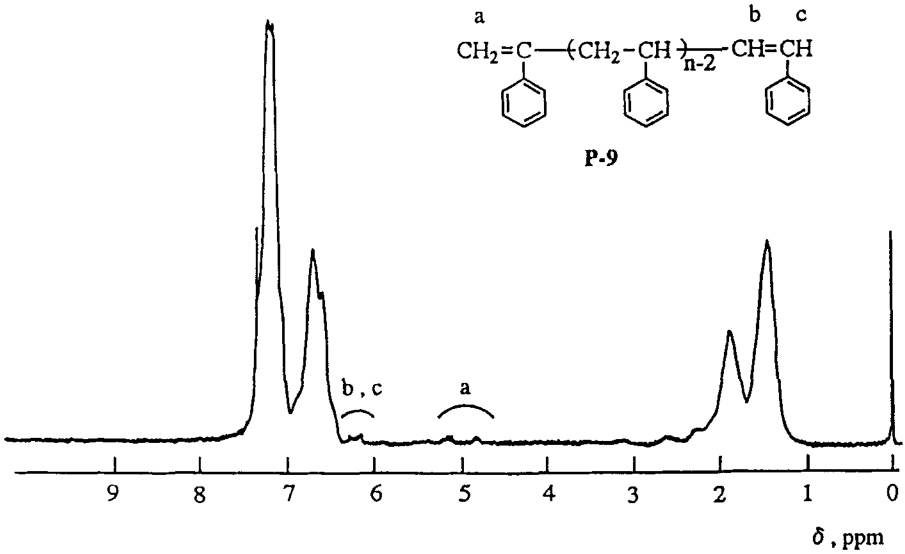


Figure 6. ^{1}H-NMR spectrum of **P-9** (200 MHz, in $CDCl_3$).

This polymer (**P-9**) is expected to work as a macromonomer, and further the interconversion of double bonds with suitable agents will produce various telechelic polymers which are important for the design of macromolecular architecture.

CONCLUSION

Diaryl diselenides such as diphenyl diselenide (**1**) and bis(*p-tert*-butylphenyl) diselenide (**2**) worked as photoiniferters for the living polymerization of styrene. The resulting polymers were telechelic polystyrenes having arylseleno groups at both chain ends. These polymers were interconverted quantitatively to polystyrenes having hydrogens and double bonds at both chain ends.

REFERENCES

[1] T. Otsu and M. Yoshida, *Makromol. Chem., Rapid Commun., 3,* 127 (1982).

[2] T. Otsu, M. Yoshida, and T. Tazaki, *Makromol. Chem., Rapid Commun., 3,* 133 (1982).

[3] K. Endo, K. Murata, and T. Otsu, *Macromolecules, 25,* 5554 (1992).

[4] T. Doi, A. Matsumoto, and T. Otsu, *J. Polym. Sci. Part A: Polym. Chem., 32,* 2911 (1994).

[5] A. Bledzki and D. Braun, *Makromol. Chem., 184,* 745 (1983).

[6] M. Oka and M. Tatemoto, *Contemporary Topics in Polymer Science*; Vol. 4, Plenum: New York, 1984; p.763.

[7] D. H. Solomon, E. Rizzardo, and P. Cacioli, Eur. Patent 135280 (1985), *Chem. Abst., 102,* 221335 (1985).

[8] J. D. Druliner, *Macromolecules, 24,* 6079 (1991).

[9] M. K. Georges, R. P. Veregin, P. M. Kazmaier, and G. K. Hammer, *Macromolecules, 26,* 2987, 5316 (1993).

[10] R. P. N. Veregin, M. K. Georges, G. K. Hammer, and P. M. Kazmeier, *Macromolecules, 26,* 4391 (1995).

[11] B. Keoshkerian, M. K. Georges, and D. Boils-Boissier, *Macromolecules, 28,* 6381 (1995).

[12] M. D. Saban, M. K. Georges, R. P. N. Veregin, G. K. Hamer, and P. M. Kazmaier, *Macromolecules, 28,* 7032 (1995).

[13] R. P. N. Veregin, P. G. Odell, L. M. Michalak, and M. K. Georges, *Macromolecules, 29,* 2746 (1996).

[14] D. Mardare and K. Matyjaszewski, *Macromolecules, 27,* 645 (1994).

[15] K. Matyjaszewski, *J. Macromol. Sci.-Pure Appl. Chem., A31,* 989 (1994).

[16] K. Matyjaszewski, S. Gaynor, and J. S. Wang, *Macromolecules, 28,* 2093 (1995).

[17] J. S. Wang and K. Matyzaszewski, *J. Am. Chem. Soc., 117,* 5614 (1995).

[18] L. Li, B. A. Howell, K. Matyjaszewski, T. Shigemoto, P. B. Smith, and D. B. Priddy, *Macromolecules, 28,* 6692 (1995).

[19] J. S. Wang and K. Matyjaszewski, *Macromolecules, 28,* 7572, 7901 (1995).

[20] K. Matyjaszewski, T. Shigemoto, J. M. J. Frechet, and M. Leduc, *Macromolecules, 29,* 4167 (1996).

[21] S. G. Gaynor, J. S. Wang, and K. Matyjaszewski, *Macromolecules, 28,* 8051 (1995).

[22] B. B. Wayland, G. Pszmik, S. L. Mukerjee, and M. Fryd, *J. Am. Chem. Soc.,116,* 7943 (1994).

[23] M. Kato, M. Kamigaito, M. Sawamoto, and T. Higashimura, *Macromolecules, 28,* 1721 (1995).

[24] T. Ando, M. Kato, M. Kamigaito, and M. Sawamoto, *Macromolecules, 29,* 1070 (1996).

[25] A. H. E. Muller, R. Zhuang, D. Yan, and G. Litvinenko, *Macromolecules, 28,* 4326 (1995).

[26] S. A. Haque and G. Clouet, *Macromol. Chem. Phys., 195,* 315 (1994).

[27] J. Kristina, G. Moad, E. Rizzardo, C. L. Winzor, C. T. Berge, and M. Fryd, *Macromolecules, 28,* 5381 (1995).

[28] G. Moad and E. Rizzardo, *Macromolecules, 28,* 8722 (1995).

[29] V. Percec and B. Barboiu, *Macromolecules, 28,* 7970 (1995).

[30] V. Percec, B. Barboiu, A. Neumann, J. C. Ronda, and M. Zhao, *Macromolecules, 29,* 3665 (1996).

[31] C. J. Hawker, *Angew. Chem. Int. Ed. Engl., 34,* 1456 (1995).

[32] C. J. Hawker and J. L. Hedrick, *Macromolecules, 28,* 2993 (1995).

[33] C. J. Hawker, E. Elece, J. Dao, W. Volksen, T. P. Russel, and G. G. Barclay, *Macromolecules, 29,* 2686 (1995).

[34] T. Fukuda, T. Terauchi, A. Goto, Y. Tsuji, T. Miyamoto, and Y. Shimidzu, *Macromolecules, 29,* 3050 (1996).

[35] T. Fukuda and T. Terauchi, *Chem. Lett., 19* (1996).

[36] W. Yang and B. Ranby, *Macromolecules, 29,* 3308 (1996).

[37] R. D. Puts and D. Y. Sogah, *Macromolecules, 29,* 3323 (1996).

[38] A. Ogawa, H. Tanaka, H. Yokoyama, R. Obayashi, K. Yokoyama, and N. Sonoda, *J. Org. Chem., 57,* 111 (1992).

[39] O. Ito, *J. Am. Chem. Soc., 105,* 850 (1983).

[40] O. Ito and M. Matsuda, *J. Am. Chem. Soc., 101,* 5732 (1979).

[41] G. A. Russell and H. Tashotoush, *J. Am. Chem. Soc., 105,* 1298 (1983).

[42] T. S. Kwon, S. Kondo, H. Kunisada, and Y. Yuki, unpublished results.

[43] K. C. Nicolaou, *Tetrahedron , 37,* 4097 (1981).

[44] D. Liotta, *Acc. Chem. Res.*, *17*, 28 (1984).

[45] S. Patai and Z. Rappoport, *The Chemistry of Organic Selenium and Tellurium Compounds*; Wiley& Sons, New York, 1986.

[46] H. J. Reich, J. M. Renga, and I. L. Reich, *J. Am. Chem. Soc.*, *97*, 5434 (1975).

[47] T. Otsu, K. Nayatani, I. Muto, and M. Imai, *Makromol. Chem.*, *27*, 142 (1955).

[48] J. Martens and K. Praefcke, *J. Organometal. Chem.*, *198*, 321 (1980).

[49] J. E. Lyons, C. H. Schiesser, and K. Sutej, *J. Org. Chem.*, *58*, 5632 (1993).

[50] B. H. Lipshutz and T. Gross, *J. Org. Chem.*, *60*, 3572 (1995).

[51] K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, *95*, 2697 (1973).

Received February 21, 1997
Revision received April 8, 1997