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

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To cite this Article Kwon, Tae Seok , Suzuki, Kirito , Takagi, Koji , Kunisada, Hideo and Yuki, Yasuo(2001) 'RADICAL POLYMERIZATION OF METHYL METHACRYLATE WITH DIPHENYL DISELENIDE UNDER THERMAL OR PHOTOIRRADIATIONAL CONDITIONS', Journal of Macromolecular Science, Part A, 38: 5, 591 — 604

To link to this Article: DOI: 10.1081/MA-100103592

URL: http://dx.doi.org/10.1081/MA-100103592

J. MACROMOL. SCI.—PURE APPL. CHEM., A38(5&6), 591–604 (2001)

RADICAL POLYMERIZATION OF METHYL METHACRYLATE WITH DIPHENYL DISELENIDE UNDER THERMAL OR PHOTOIRRADIATIONAL CONDITIONS

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ABSTRACT

Polymerization of methyl methacrylate (MMA) with diphenyl diselenide (**DPDSE**) in the presence of AIBN at 60°C was investigated. **DPDSE** was worked as a chain transfer agent (CTA). The chain transfer constant (C_{tr}) of **DPDSE** for MMA was estimated to be 1.43. On the other hand, **DPDSE** was functioned as a photoiniferter for the photopolymerization of MMA. In a limited range of conversion, both the polymer yield and number average of molecular weight ($\overline{M}_n$) increased with the reaction time, and the $\overline{M}_n$ linearly increased with the yield. The terminal structure of poly(MMA) was investigated by the ^{77}Se NMR spectrum based on Methyl α-phenylseleno isobutylate (**MSEPI**) as model compound of the ω-chain end of poly(MMA). Further, photopolymerization of poly (MMA) containing phenylseleno group at ω-chain end as a polymeric photoiniferter with MMA effectively afforded a poly (MMA) having higher molecular weight.

Key Words: Radical polymerization; Diphenyl diselenide; Chain transfer agent; Photoiniferter; Methyl α-phenylseleno isobutylate; Polymeric photoiniferter.

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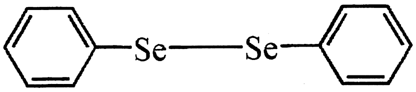
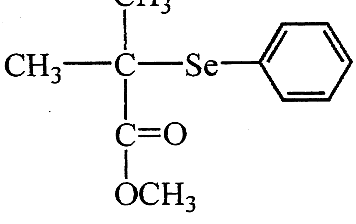
INTRODUCTION

In previous papers, we reported that the **DPDSE** was worked as a chain transfer agent (CTA) in polymerization of styrene under thermal conditions [1]. On the other hand, we have been reported the preparation of well-defined polymers using organic selenium compounds, such as **DPDSE**, benzyl phenyl selenide, or 1,4-bis (*p*-tert-butylphenylselenomethyl) benzene as photoiniferter in polymerization of styrene under photoirradiational condition [2–4]. It was based upon the phenylseleno radical which derived from homolytic cleavage on photoirradiation of **DPDSE** or alkyl phenyl selenides are very stable, the reactivity towards carbon-carbon double bonds, and having large chain transfer abilities [5–9]. From this method, we could obtain the polymers having phenylseleno group at one or both chain ends. Moreover, polymers containing various end groups can be prepared by interconversion of phenylseleno group with an elimination reaction under mild conditions [10, 11]. More recently, we have performed a synthesis of block and graft copolymers with styrene or *p*-substituted styrene monomers basis on this method [12–14]. This 'iniferter method' is well known to be a very useful means in several methods for the synthesis of a controlled polymer. Otsu *et al.* had already reported that tetraethylthiuram disulfide worked as an iniferter in thermal or photopolymerization [15]. They also reported that dithio-



DPDSE



MSEPI

Structure 1.

carbamate derivatives, such as benzyl *N,N*-diethyldithiocarbamate, benzyl *N*-ethyldithiocarbamate, *p*-xylylene bis (*N,N*-diethyldithiocarbamate), *p*-xylylene bis (*N*-ethyldithiocarbamate), 1,2,4,5-tetrakis (*N,N*-diethyldithiocarbamylmethyl) benzene as photoiniferters for the polymerization of vinyl monomers [16–19]. These compounds that acted as initiator, have a high reactivity for chain transfer and termination by way of a primary radical in radical polymerization. The resulting polymers, which were prepared by this method, have iniferter fragments at chain ends. They can be applied to the preparation of various types of polymers [20–22].

In this paper, we describe the polymerization of MMA with **DPDSE** as a CTA or photoiniferter as a series of polymerization of vinyl monomers using organic selenium compounds. The terminal group analysis of resulting poly(MMA) was carried out by reference to **MSEPI** as a model compound of ω-chain end in poly (MMA). The chain extension with the functional poly(MMA) having phenylseleno group at ω-chain end as polymeric photoiniferter has been also investigated.

EXPERIMENTAL

Materials

DPDSE was prepared according to the previous paper [2]. MMA was washed with aqueous alkaline solution and water, and distilled over calcium hydride just before use. 2,2’-Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol. Solvents were purified by distillation after the appropriate drying. Phenylselenenyl chloride (**PSECl**) and other reagents were obtained commercially and used without further purification.

Synthesis of MSEPI

To a stirring solution of diisopropylamine (2.1 mL, 15 mmol) in THF (15 mL), a solution of n-BuLi (9.74 mL, 15 mmol) in n-hexane (1.54 mol/L) was added slowly at 0°C, and stirring was continued for an additional 0.5 hour. After cooling to –78°C, methyl isobutylate (1.72 mL, 15 mmol) is added, and further stirring occurred for 0.5 hour. Then, to this reaction mixture, a solution of PSECl (2.87 g, 15 mmol) in THF (20 mL) was added slowly. After stirring for 10 hours, the reaction mixture was poured into ammonium chloride (10.7 g, 0.2 mol) in water (40 mL) and the organic layer was separated. The aqueous layer was extracted with dietyl ether. The organic layer and extracts were combined, washed with water, 5% sodium chloride aqueous solution, and dried over anhydrous potassium sulfate. After evaporation of solvent, the residue was separated with column chromatography (Wakogel C-200, n-hexane/methylene chloride = 6:4). The resulting product was recrystallized with n-hexane. The yield was 0.5 g (14.0%). mp 51°C.

^{1}H-NMR (400 MHz, in $CDCl_3$): $\delta = 1.58$ (s, $2CH_3$, 6H), 3.63 (s, OCH_3, 3H), and 7.26–7.58 ppm (C_6H_5, 5H).

^{13}C-NMR (100 MHz, in $CDCl_3$): $\delta = 26.1$ (CH_3), 45.3 (C-Se), and 51.8 ppm (OCH_3). ^{77}Se-NMR (76.3 MHz, in $CDCl_3$): $\delta = 556.2$ ppm.

IR (KBr): n = 1475.3, 1575.6, 1724.1, 2360.4, 2859.9, 2948.6, and 2993.0, 3056.6 cm^{-1} UV (ethanol): $\lambda_{max} = 266$, ($\varepsilon = 814.22$).

Polymerization of MMA with DPDSE in the Presence of AIBN

The required amounts of AIBN, **DPDSE**, and 5 mL of MMA 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. 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.

Photopolymerization of MMA with DPDSE

DPDSE (0.015 g, 0.047 mmol) and MMA (5 mL) 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 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 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.

Irradiation of MSEPI

A solution of MSEPI (0.5 mmol) in benzene (2.5 ml) was charged into a Pyrex tube. The tube was degassed under vacuum by the conventional freeze and thaw technique, and sealed off under vacuum. It was irradiated with a 100W high-pressure mercury lamp for 15 hours at room temperature. After evaporation of the solvent, the residue was dried in vacuum.

Photopolymerization of MMA with P-2 as a Polymeric Photoiniferter

A sample of P-2 (0.6 g), MMA (9 mL) and benzene (6 mL) was divided equally into three polymerization tubes. These solutions were irradiated with a high-pressure mercury lamp from a 8 cm distance at room temperature. At approximate intervals, the reaction mixtures were poured into hexane. The resulting polymers were dried in vacuum. The yield of polymers was determined from the weight of the dried polymers obtained.

Measurements

IR spectra were measured by a Nicolet Impact-400D. ^{1}H– and ^{13}C-NMR spectra were recorded by a Jeol JNM–GX400 spectrometer at 400 MHz in $CDCl_3$ with tetramethylsilane (TMS) as an internal reference. ^{77}Se-NMR spectrum was determined on a Varian UNITY plus-400 spectrometer at 76.3 MHz in $CDCl_3$ with **DPDSE** as an internal reference. Gel permeation chromatography (GPC) was performed on a TOSOH DP-8020 with GMH TSK gel-columns and a differential refractometric detector in tetrahydrofuran. The molecular weights were determined using polystyrene standards.

RESULTS AND DISCUSSION

Polymerization of MMA in the Presence of DPDSE at 60°C

To investigate the behavior of **DPDSE** under thermal condition, polymerization of MMA was carried out at 60°C under sealed conditions in the presence of AIBN as the initiator. This polymerization was performed at constant AIBN concentration, while the ratio of **DPDSE** to monomer was varied. The polymerization was carried out keeping the yield of polymer below 5%. The results are shown in Table 1. The $\overline{M}_n$ of the resulting polymers was markedly lower than that of polymer obtained in the absence of **DPDSE**. The recovery of polymers precipitated in methanol and the $\overline{M}_n$ of the polymers decreased with the increasing of the amount

Table 1. Radical Polymerization of MMA[a] with Diphenyl Diselenide **(DPDSE)** in the Presence of AIBN[b] at 60°C

Run	[**DPDSE**] / [MMA] × 10^3	Time h	Yield[c] %	$\overline{M}_n$[d]	$\overline{M}_w \overline{M}_n$
1	0	1	4.9	494,800	4.01
2	1.07	1	2.9	38,900	1.74
3	2.14	2	3.6	26,200	1.69
4	3.21	3	3.4	20,500	1.54
5	4.28	3	0.7	14,900	1.34

[a] MMA = 5 mL.

[b] AIBN = 0.01 mmol.

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

[d] Estimated by GPC.

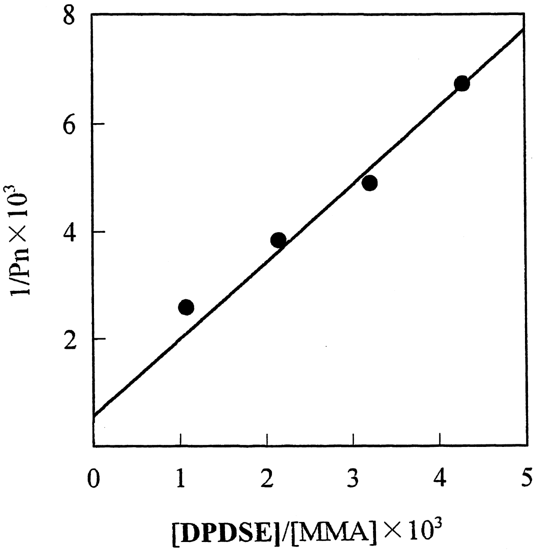


Figure 1. The Mayo plot for the polymerization of MMA with **DPDSE**. [MMA] = 46.8 mmol, [AIBN] = 0.01 mmol.

of **DPDSE**. This means that **DPDSE** works as an initiator, but chain transfer agent (CTA) only in this polymerization.

In Figure 1, the C_{tr} value was obtained by the slope from the linear plot of $1/P_n$ of the polymers vs. the concentrations of **DPDSE** to monomer according to the Mayo's Equation 1 [23] as follows:

$$1/P_n = 1/P_o + C_{CTA}\,[CTA]/[M] + C_S[S]/[M] + C_I[I]/[M] + C_M \quad (1)$$

where, P_o and P_n are the degree of polymerization in the absence and presence of the CTA, respectively. The C_S, C_I, C_M and C_{CTA} are the chain transfer constant (C_{tr}) to solvent, initiator, monomer and CTA, respectively. For the bulk polymerization, C_S of solvent is 0, C_I of AIBN is 0, and C_M of MMA is 0.07~0.18 × 10^{-4} [24], which are negligibly small compared with that of common CTA. Therefore, Equation 1 can be given by the following expression (Equation 2):

$$1/P_n \fallingdotseq 1/P_o + C_{tr}\,[CTA]/[M] \quad (2)$$

From the slope of this straight line in Figure 1, the C_{tr} of **DPDSE** was evaluated to be 1.43. This value is remarkably higher than that of diphenyl disulfide (8.5 × 10^{-3}) as a representative CTA [25]. This result coincided with the fact that **DPDSE** undergoes the SH2 reaction by an alkyl radical approximately 160-fold faster than diphenyl disulfide [26]. It is also revealed that **DPDSE** shows a very high radical capturing ability and control ability for the terminal group of polymer main chain.

Photopolymerization of MMA in the Presence of DPDSE

In order to investigate the behavior of **DPDSE** under photoirradiational conditions, the polymerization of MMA was carried out with various concentration of **DPDSE** to MMA without solvent under irradiation of a high-pressure mercury lamp at room temperature. The results are presented in Table 2.

These polymerizations proceeded smoothly in the presence of **DPDSE**, but scarcely provided polymers in the absence of **DPDSE**. Moreover, the $\overline{M}_n$ decreased with the increasing amount of **DPDSE**. These results suggest that **DPDSE** not only works as a photoinitiator but also functions as a CTA, and the ability of chain transfer is very high as mentioned above. On the other hand, the relationships between the reaction times and polymer yield and $\overline{M}_n$ were investigated on the photopolymerization of MMA with **DPDSE** (0.001 molar equivalent relative to the monomer). The polymer yields and $\overline{M}_n$ values of the resulting polymers were found to increase with the reaction time as shown in Table 3. Furthermore, almost linear relationship of plot was observed for $\overline{M}_n$ value vs. the polymer yield as shown in Figure 2. These results indicate that the terminal end of the resulting poly(MMA) were activated with seleno groups.

Figure 3 shows the ^{1}H-NMR spectrum of P-1. The signal due to phenyl protons (g) at 7.21–7.53 ppm was observed weakly. The end group functionality was obtained by comparing $\overline{M}_n$ from GPC with the peak intensity ratio of the phenyl protons signal to methoxy signal (d) at 3.59 ppm. It was calculated as 0.6 (this value was reproducible to about ± 10% on repeated runs). Two kinds of methylene signals ((c) and (b)) were observed at 2.47 and 1.87–2.10. Furthermore, signals due to methylene protons ((e) and (f)) of vinylidene group from disproportionation reaction [27] were observed at 5.47 and 6.21 ppm different from those in the MMA monomer at 5.58 and 6.11 ppm. These results indicate that poly(MMA) having a complex structure with phenylseleno group at one or both chain ends is due to the very slow initiation of **DPDSE** in the early step of this polymerization. On the other hand, from the signals of methyl group (a) at 0.82,1.01, and

Table 2. Photopolymerization of MMA in the Presence of Diphenyl Diselenide **(DPDSE)** Using a 100 W High Pressure Hg Lamp at Room Temperature

Run	[**DPDSE**]/[MMA][a]	Time h	Yield[b] %	$\overline{M}_n$[c]	$\overline{M}_w\overline{M}_n$
1	0	2	1.1	1,780,000	2.11
2	0.0001	2	16.0	29,200	2.82
3	0.0002	2	20.6	42,200	2.08
4	0.001	2	26.0	11,500	2.55
5	0.002	2	34.1	10,900	2.55

[a] MMA = 5 mL.

[b] Recovery of polymer which was insoluble part to n-hexane.

[c] Estimated by GPC.

Table 3. Photopolymerization of MMA in the Presence of **DPDSE**[a]

Polymer	Time h	Yield[b] %	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$
P-1	1.0	9.4	7,100	1.96
P-2	2.0	18.2	11,500	2.55
P-3	2.5	20.3	11,700	2.69
P-4	3.0	24.1	12,900	2.90
P-5	3.5	27.1	14,400	3.00
P-6	4.0	30.5	16,100	3.05

[a] Conditions: 5 mL of MMA and 0.015 g of **DPDSE** ([**DPDSE**]/[MMA] = 0.001) were irradiated at room temperature.

[b] Recovery of polymer which was insoluble part to n-hexane.

[c] Estimated by GPC.

1.28–1.42 ppm, the tacticity of poly(MMA) is estimated to be rr/mr(rm)/mm: 63/26/11. These values are very close to the one prepared using a typical free radical initiator [28].

Irradiation to MSEPI

To investigate the structure of ω-chain end of poly(MMA) in the early step of polymerization, a solution of **MSEPI** (0.5 mmol), as a model compound of ω-

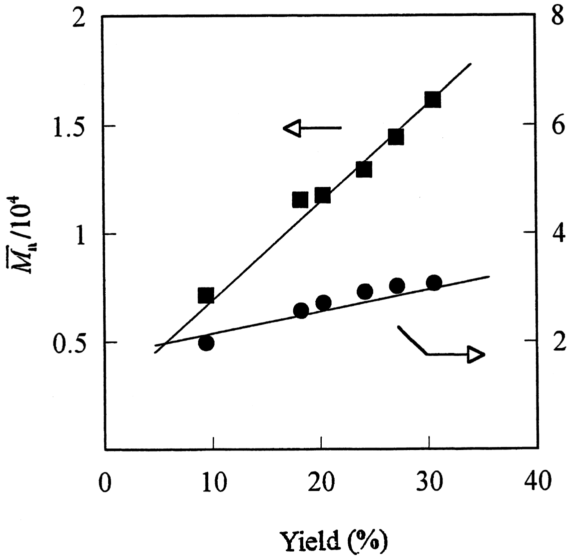


Figure 2. Yield - $\overline{M}_n$ (■) and yield - $\overline{M}_w/\overline{M}_n$ (•) relations in photopolymerization of MMA with DPDSE as a phopoiniferter. [MMA] = 46.8 mmol, [**DPDSE**]/[MMA] = 0.001.

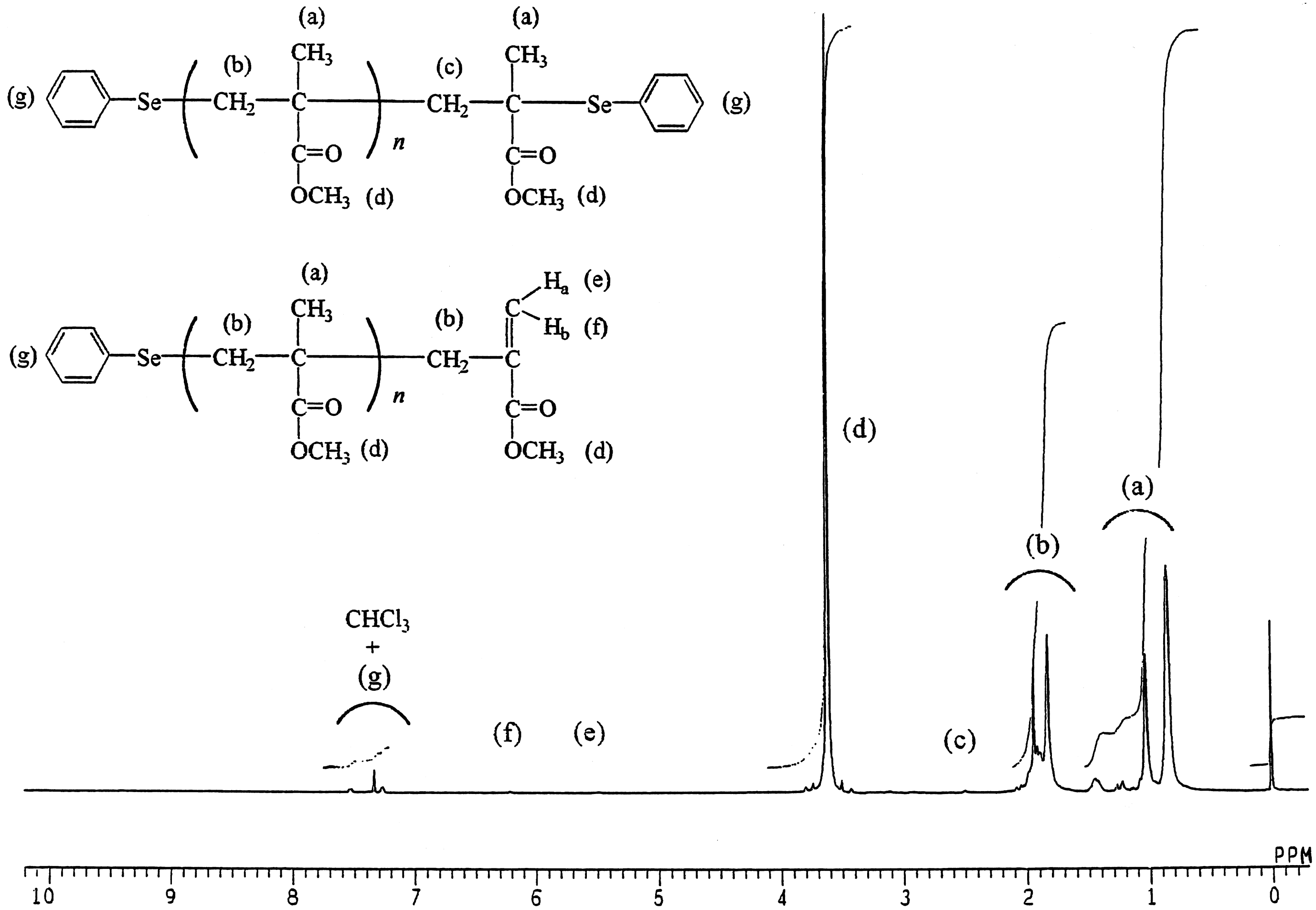


Figure 3. ^{1}H NMR spectrum (400 MHz, in CDCl$_3$) of P-1 ($\overline{M}_n = 7{,}100, \overline{M}_w/\overline{M}_n = 1.96$).

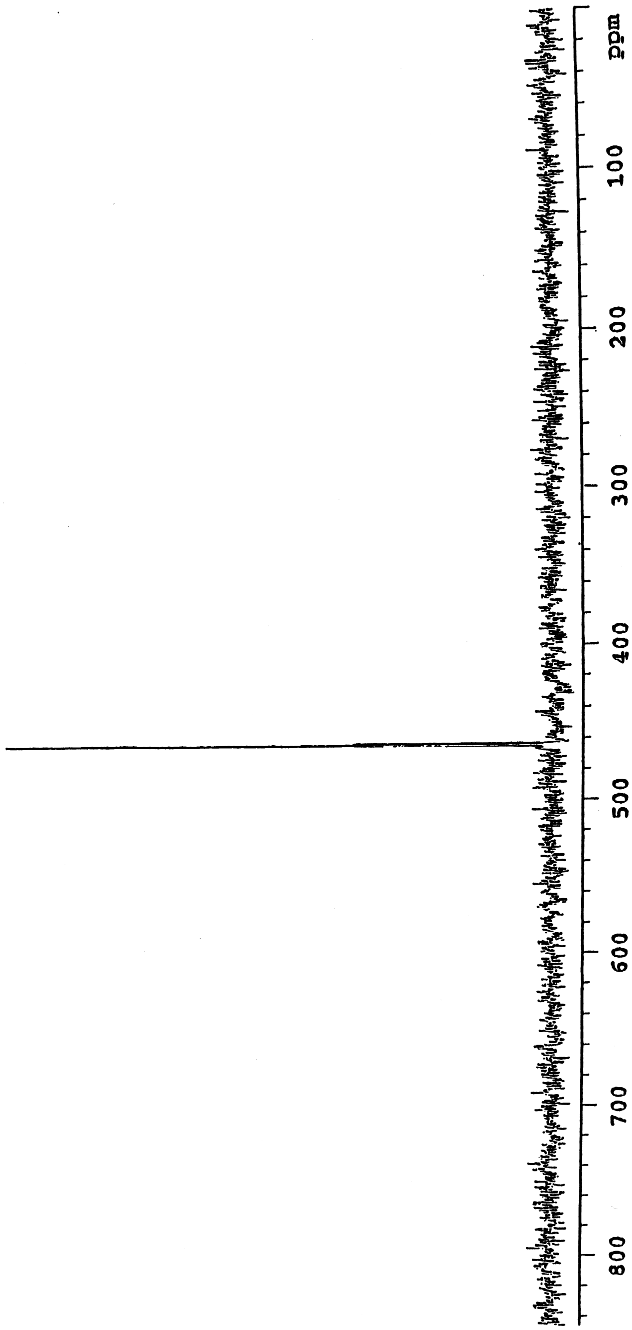


Figure 4. ^{77}Se NMR spectrum (76.3 MHz, in $CDCl_3$) of photoirradiated MSEPI.

chain end in poly (MMA) in benzene (2.5 ml), was irradiated with a 100W high-pressure mercury lamp for 15 hours at room temperature. ^{77}Se-NMR spectrum of the resulting compound is shown in Figure 4. The signal from **MSEPI** at 556.2 ppm completely disappeared. A signal due to **DPDSE** can be seen at 464.8 ppm. This result indicates that the complicated structure in ω-chain end of poly(MMA) occurred by a coupling reaction of phenylseleno radicals with each other. The further study for a mechanism of polymerization and the terminal structure of poly(MMA) are in progress, and will be reported in the near future.

Photopolymerization of MMA with P-2 as a Polymeric Photoiniferter

In order to confirm the structure of the phenylseleno chain end, a chain extension experiment was carried out with 0.2 g of **P-2**, and 3 mL of MMA was dissolved in 2 mL of benzene solution under photoirradiational conditions. Both the polymer yields and the $\overline{M}_n$ increased with the irradiation time as shown in Table 4. The values of IE were approximately 0.82–0.99. Furthermore, the numbers of molecules (NM) of the resulting poly(MMA) were unaltered ($1.05–1.27 \times 10^{19}$). The constant NM independence of the polymerization suggests that the poly(MMA) has an activated ω-chain end due to the phenylseleno group. These results also indicate that **P-2** worked as a polymeric photoiniferter effectively. Moreover, $\overline{M}_n$ values of the resulting polymers increased linearly with polymer yields as seen from Figure 5. These values were in fair agreement with the calculation values. On the other hand, Figure 6 shows the GPC curves of **P-2** and **p-9**. The unimodal in GPC curve of **P-9** shifted to the higher molecular weight region in comparison with **P-2**. From above results, we thought that **P-2** would effectively

Table 4. Photopolymerization of MMA with P-2 as a Polymeric Photoiniferter[a]

Polymer	Time h	Yield[b] (g)	Conversion[c] (%)	$\overline{M}_{n,\,calc}$[d]	$\overline{M}_{n,\,GPC}$[e]	$\overline{M}_w/\overline{M}_n$	IE[f]	NM[g] $\times 10^{-19}$
P-2	0	0.20	0	—	11,500	2.55	—	1.05
P-7	2	0.54	12.24	16,200	19,700	2.32	0.82	1.05
P-8	4	0.79	20.96	27,700	27,900	1.98	0.99	1.27
P-9	5	0.82	22.01	29,100	29,300	2.17	0.99	1.27

[a] Conditions : 3 mL of MMA, 0.2 g of **P-2** ([**P-2**]/[MMA] = 7.56×10^{-4}), and 2 mL of benzene were irradiated at room temperature.

[b] Recovery of polymer which was insoluble part to n-hexane.

[c] [(Weight of precipitated polymer—Weight of polymeric photoiniferter)/Weight of charged MMA] × 100.

[d] $([MMA]_0/[\textbf{P-2}]_0 \times MW_{MMA} \times \text{Yield}$.

[e] Estimated by GPC.

[f] Initiator Efficiency = $\overline{M}_{n,\,calc}/\overline{M}_{n,\,GPC}$.

[g] Number of Molecules = [Yield (g)/Number average molecular weight] × (6.023×10^{23}).

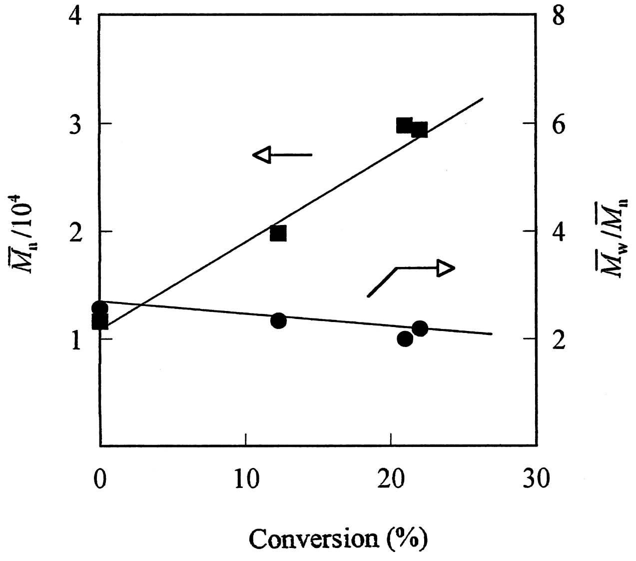
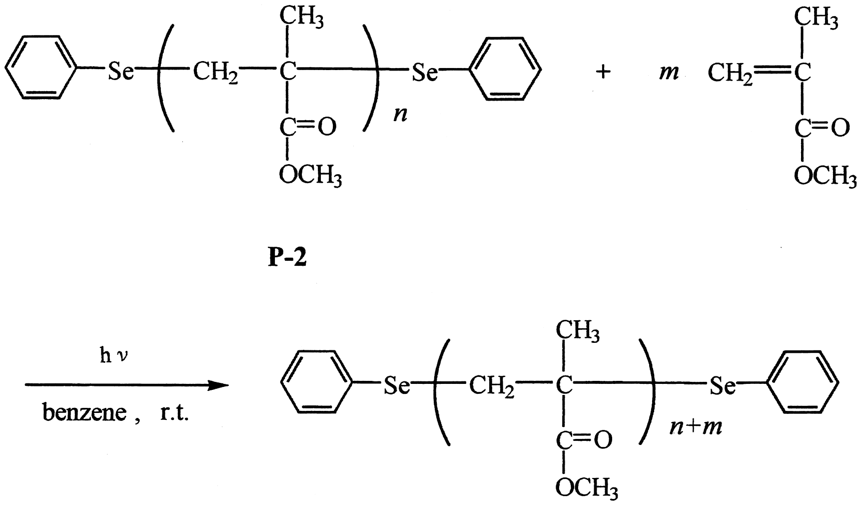


Figure 5. Conversion-$\overline{M}_n$ (■) and Conversion -$\overline{M}_w/\overline{M}_n$ (•)- M_w/M_n relations in photopolymerization of MMA with **P-2** as a polymeric photoiniferter. [MMA] = 28.1 mmol, [**DPDSE**]/[MMA] = 7.56×10^{-4}.

function as a polymeric photoiniferter for the photopolymerization of MMA to produce the corresponding polymers as shown in Equation 3.



(3)

From the above results, this functional poly(MMA) having a phenylseleno group at chain ends is expected to work as a precursor for the design and control of polymer structure.

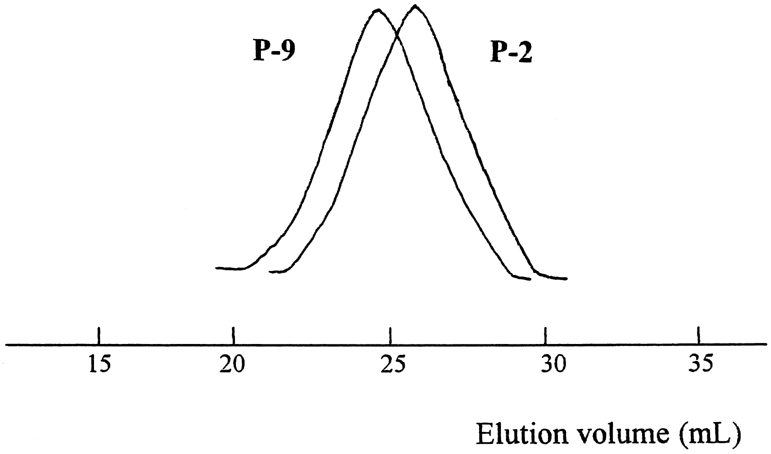


Figure 6. GPC curves of **P-2** (M_n =11,500, M_w/M_n= 2.55) and **P-9** ($\overline{M}_n$ = 29,300, $\overline{M}_w/\overline{M}_n$ = 2.17).

CONCLUSION

DPDSE worked as a CTA in polymerization of MMA in the presence of AIBN at 60°C, and the C_{tr} was estimated to be 1.43. **DPDSE** also worked as a photoiniferter for photopolymerization of MMA. The polymer yields and the $\overline{M}_n$ of the polymers increased with reaction time. The terminal structure of poly(MMA) was investigated with the ^{77}Se NMR spectrum of Methyl α-phenylseleno isobutylate (**MSEPI**) as a model compound of the ω-chain end of poly(MMA). Furthermore, by the irradiation of the resulting polymer as a polymeric photoiniferter in MMA, poly(MMA) with a higher molecular weight was obtained.

ACKNOWLEDGMENT

This work was supported by a grant-in-aid for Scientific Research (No. 10650865) from the Ministry of Education, Science, Sports, and Culture of Japan.

REFERENCES

1. Kwon, T.S.; Kondo, S.; Kunisada, H.; Yuki, Y. Eur. Polym. J., **1999**, *35(4)*, 727.
2. Kwon, T.S.; Kumazawa, S.; Yokoi, T.; Kondo, S.; Kunisada, H.; Yuki, Y. Journ. Mac. Sci., Pure and Appl. Chem. **1997**, *A34*, 1553.
3. Kwon, T.S.; Kondo, S.; Kunisada, H.; Yuki, Y. Polym. J., **1998**, *30*, 559.
4. Kwon, T.S.; Kumazawa, S.; Kondo, S.; Takagi, K.; Kunisada, H.; Yuki, Y. Journ. Mac. Sci., Pure and Appl. Chem. **1998**, *A35(12)*, 1895.
5. Ogawa, A.; Tanaka, H.; Yokoyama, H.; Obayashi, R.; Yokoyama, K.; Sonoda, N. J. Org. Chem., **1992**, *57*, 111.
6. Nicolaou, K.C. Tetrahedron. **1981**, *37*, 4097.

7. Sharpless, K.B.; Lauer, R.F.J. Am. Chem. Soc. **1973**, *95,* 2697.
8. Russell, G.A.; Tashotoush, H. J. Am. Chem. Soc. **1983**, *105*, 1298.
9. Patai, S.; Rappoport, Z. The Chemistry of Organic Selenium and Tellurium Compounds; Wiley: New York, 1986.
10. Gutierrez, C.G.; Stringham, R.A.; Nitasaka, T.; Glasscock, K.G. J. Org. Chem.. **1980**, *45,* 3393.
11. Sharpless, K.B.; Young, M.W.; Lauer, R.F. Tetrahedron Letters. **1973**, *22,* 1979.
12. Kwon, T.S.; Ochiai, H.; Kondo, S.; Takagi, K.; Kunisada, H.; Yuki, Y. Polym. J. **1999**, *31,* 411.
13. Kwon, T.S.; Kondo, S.; Takagi, K.; Kunisada, H.; Yuki, Y. Polym. J. **1999**, *31,* 483.
14. Kwon, T.S.; Kondo, S.; Takagi, K.; Kunisada, H.; Yuki, Y. Journ. Mac. Sci., Pure and Appl. Chem. **2000**, *A37(11)*.
15. Otsu, T.; Yoshida, M. Makromol, Chem., Rapid Commun. **1982**, *3*, 127.
16. Otsu, T.; Kuriyama, A. J. Macromol. Sci. Chem. **1984**, *A21*, 961.
17. Otsu, T.; Yoshida, M.; Kuriyama, A. Polym. Bull. **1982**, *7*, 45.
18. Kuriyama, A.; Otsu, T. Polym. J., **1984**, *16(6)*, 511.
19. Otsu, T.; Kuriyama, A. Polym. J., **1985**, *17(1)*, 97.
20. Otsu, T.; M. Yoshida, Polym. Bull., **1982**, *7*, 197.
21. Otsu, T.; Kuriyama, A. Polym. Bull., **1984**, *11*, 135.
22. Doi, T.; Matsumoto, A.; Otsu, T. J. Polym. Sci., **1994**, *32*, 2911.
23. Mayo, F.R. J. Am. Chem. Soc., **1943**, *65,* 2324.
24. Berger, K.C.; Brandrup, G. *Polymer Handbook*, 3rd Edn.; Brandrup Wiley: New York, 1989, 85–91.
25. Otsu, T.; Kinoshita, Y.; Imoto, M. Makromol. Chem. **1964**, *73*, 225.
26. Russell, G.A.; Tashtoush, H. J. Am. Chem. Soc. **1983**, *105*, 1398.
27. Hatada, K.; Kitayama, T.; Masuda, E. Polym. J. **1986**, *18(5)*, 395.
28. Bovey, F.A.; Tiers, G.V.D. J. Polym. Sci., **1960**, *44*, 173.

Received July 30, 2000
Revision received November 20, 2000