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SYNTHESIS OF MACROMONOMER USING END FUNCTIONAL POLYSTYRENE PREPARED FROM *p*-METHOXYBENZYL *p*-TRIMETHYL-SILYLPHENYL SELENIDE AS A PHOTOINIFERTER

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SYNTHESIS OF MACROMONOMER USING END FUNCTIONAL POLYSTYRENE PREPARED FROM *p*-METHOXYBENZYL *p*-TRIMETHYLSILYLPHENYL SELENIDE AS A PHOTOINIFERTER

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Key Words: *p*-Methoxybenzyl *p*-Trimethylsilylphenyl Selenide, Photoiniferter, Radical Polymerization, End Functional Polystyrene, Macromonomer, Graft Copolymer

ABSTRACT

The end functional polystyrene having phenylseleno group at ω-chain end was prepared from radical polymerization of styrene in the presence of *p*-methoxybenzyl *p*-trimethylsilylphenyl selenide as a photoiniferter. The phenylseleno group at ω-chain end in polystyrene was eliminated by hydrogen peroxide. The resulting polystyrene was interconverted quantitatively to polystyrene having epoxy end group by the oxidation with *m*-chloroperbenzoic acid. The macromonomer having a meth-acryloyl end group was synthesized from polystyrene containing epoxy end group with methacrylic acid in xylene at 140°C. Copolymerization of this macromonomer with methyl methacrylate afforded effectively a graft copolymer composed of a poly(methyl methacrylate) backbone and polystyrene branches.

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INTRODUCTION

The importance of the synthesis of well-defined graft copolymers has been increased for the design of various functional materials. For this purpose, the macromonomer method is well known as one of the most useful methods among the several grafting methods because the number and length of branch segments of graft copolymer can be controlled [1-5]. Various research has reported for the synthesis [6-10] and polymerization behavior [11-13] of macromonomers, and for application for the preparation of graft copolymers [14-17]. These researches reveal that the success in synthesis of well-defined graft copolymers depends upon well-controlled macromonomer. Otsu *et al*. [18] also reported for the livingness of the polymerization using well designed photoiniferter.

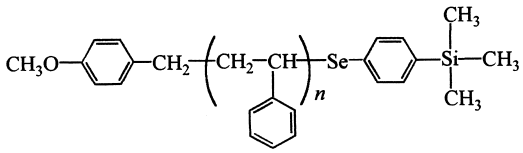
We reported the synthesis of well-controlled polymers in the presence of selenium compound as photoiniferter [19-21]. It takes advantage of high end capping abilities of seleno radical. For example, benzyl phenyl selenide works as a photoiniferter and afford an end functional polystyrene having seleno group at ω-main chain end [22]. The resulting polystyrene also works as polymeric photoiniferter and affords various types of block copolymers. Recently, we also reported the synthesis of functional polymers carrying terminal epoxy group by conversion of end groups [23]. We expect the synthesis of macromonomer by end functional polymer and it's application.

This paper describes the synthesis of macromonomer (**PSMAC**) using well-controlled polystyrene (**MTBPSE-PST**) prepared from *p*-methoxybenzyl *p*-trimethylsilylphenyl selenide as a photoiniferter. Application for the synthesis of graft copolymer by copolymerization of **PSMAC** with methyl methacrylate is also investigated.

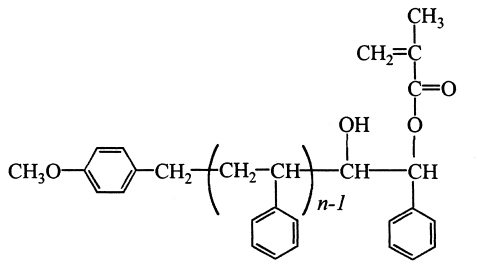
EXPERIMENTAL

Materials

Styrene (St), methacrylic acid (MAA), and methyl methacrylate (MMA) were purified and distilled by ordinary method just before use. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol. *p*-Methoxybenzyl *p*-trimethylsilylphenyl selenide (MTBPSE) was prepared as in a previous paper [22]. Solvents were purified by distillation after appropriate drying. Other reagents were obtained commercially and used without further purification.



MTBPSE-PST



PSMAC

Synthesis of ω-End Functional Polystyrene with MTBPSE

A solution of MTBPSE (0.24 g) in styrene (8 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 3 hours. The tube was opened and contents were poured into methanol. The resulting polystyrene (MTBPSE-PST) was reprecipitated from methylene chloride in methanol. Yield was 1.12 g (15.5%).

Synthesis of MTBPSE-PSO by Oxidative Elimination of MTBPSE-PST

A solution of **MTBPSE-PST** (2.5 g) and 30% aqueous hydrogen peroxide (5.6 g) in THF (45 ml) was stirred for 1 week at room temperature. After evaporation of most of the THF, the residue was poured into methanol to precipitate the polymer. The polymer (**MTBPSE-PSO**) was purified by reprecipitation from THF in methanol, followed by drying in vacuum. Yield was 2.33 g (93.2%).

Synthesis of MTBPSE-PSE by Epoxidation of MTBPSE-PSO

To a solution of *m*-chloroperbenzoic acid (6.5 g) in methylene chloride (150 ml), **MTBPSE-PSO** (1.0 g,) was added at 0°C. After the reaction mixture was stirred for 24 hours at 0°C, an aqueous solution of sodium thiosulfate (100 ml) and an aqueous solution of sodium hydrogen carbonate (100 ml) were added, and stirred for an additional 2 hours 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 (**MTBPSE-PSE**) was reprecipitated from benzene with methanol, and dried in vacuum. The yield was 0.91 g (91.0%)

Synthesis of Macromonomer

A solution of **MTBPSE-PSE** (3.0 g), methacrylic acid (72.0 g), N,N-dimethyl n-dodecyl amine (1.2 g), and hydroquinone (0.12 g) in xylene (12 g) was reacted for 7 hours at 140°C. The reaction mixture was poured into methanol to precipitate the polymer. The polymer (**PSMAC**) was purified by reprecipitation from THF with methanol, followed by drying in vacuum. Yield was 2.88 g (96.0%).

Homopolymerization of PSMAC

A solution of **PSMAC** (0.1 g) and AIBN (0.0008 g) in benzene (1.0 ml) was prepared in an ample tube. The polymerization was carried out for 1 week at 60°C. The tube was degassed under vacuum by the conventional freeze and thaw technique, and sealed under vacuum. After polymerization, the mixture was poured into a large amount of methanol to precipitate the polymer. The resulting polymer (**HPSMAC**) was then reprecipitated from benzene with methanol, followed by drying in vacuum.

Synthesis of Graft Copolymer from PSMAC with MMA

PSMAC (0.1 g), AIBN (0.06 g), MMA (2 ml), and benzene (2 ml) in Pyrex tube was reacted for 6 hours at 60°C in the case of **PMMA-g-PST-1**. The resulting polymer mixture was poured into methanol. 0.4 g of isolated polymer was dissolved in 20 ml of benzene. The fractionations were carried out by adding 4 ml portions of methanol and centrifuging off. The isolated polymers were examined by GPC and ^{1}H-NMR analysis. The resulting graft copolymer was dried in vacuum. The polymer fractions thus extracted were examined by ^{1}H-

NMR analysis. In other cases, graft copolymers were prepared with the same method.

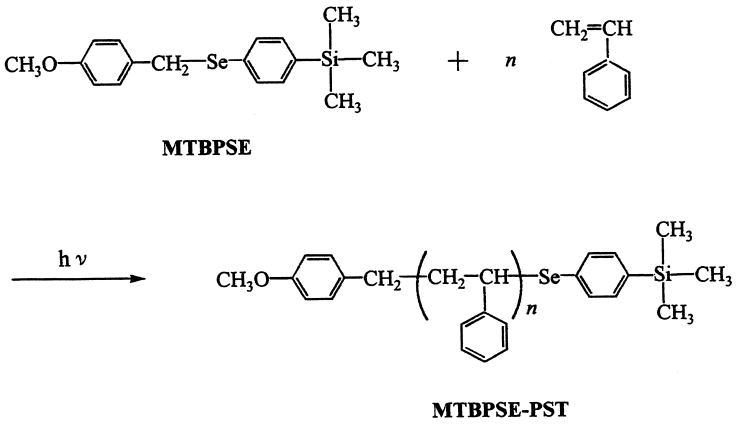
Measurements

^{1}H-NMR spectra were recorded by a JEOL JNM-GX400 (400MHZ) 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.

RESULTS AND DISCUSSION

Photopolymerization of Styrene with MTBPSE

Polymerization was carried out by photoirradiation of styrene with **MTBPSE** at room temperature (Scheme 1). $\overline{M}_n$'s of resulting polymer (**MTBPSE-PST**) are 4,800 ($\overline{M}_w/\overline{M}_n$ = 1.54) by GPC and 4850 by the signal intensity ratio of the methoxy protons (c) to polystyrene (d+e) in ^{1}H-NMR spectrum (Figure 1), respectively. On the other hand, signals due to trimethylsilyl and methoxy groups were observed at 0.25 and 3.72 ppm in ^{1}H-NMR spectrum of the **MTBPSE-PST**, respectively. The signal intensity ratio of the trimethylsilyl pro-



Scheme 1.

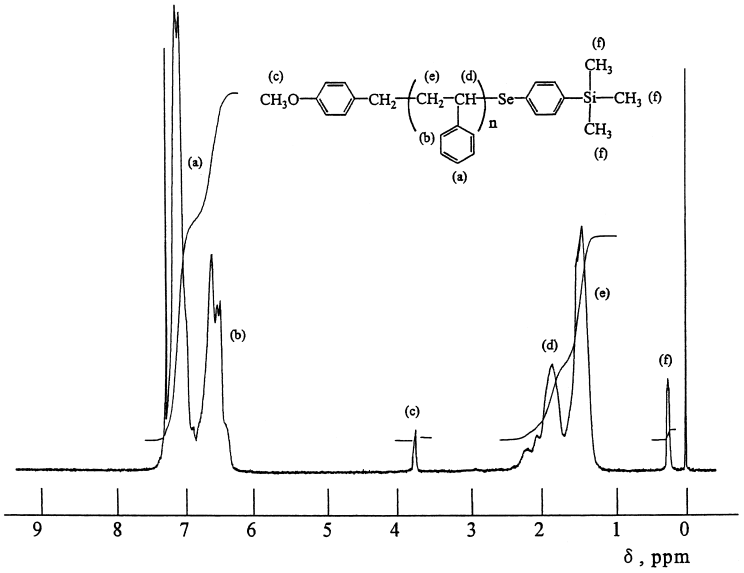
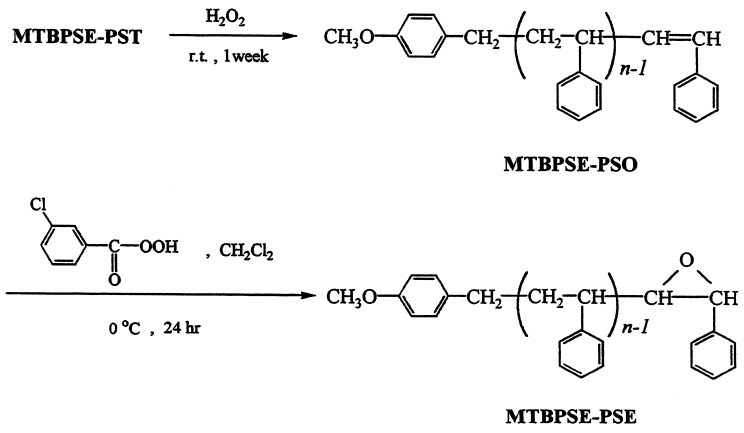


Figure 1. ^{1}H NMR spectrum (400MHz, in $CDCl_3$) of **MTBPSE-PST**.

tons (f) to the methoxy protons (c) of polystyrene was approximately 3. From this result, the degree of functionality (DF) was calculated as 0.95. This value was reproducible within about ±5% on repeated runs. This indicates that end functional polystyrene containing phenylseleno group at ω-chain end was successfully prepared.

Synthesis of MTBPSE-PSO and MTBPSE-PSE

Polystyrene having carbon-carbon double bond or epoxy group at ω-chain end were prepared thanks to a specific characteristic of the selenium compound [24] (Scheme 2). The results of yields of **MTBPSE-PSO** ($\overline{M}_n$ = 4,100, $\overline{M}_w/\overline{M}_n$ = 1.50) or **MTBPSE-PSE** ($\overline{M}_n$ = 5,800 $\overline{M}_w/\overline{M}_n$ = 1.44) are 93.2% or 91.0%, respectively. ^{1}H-NMR spectrum of **MTBPSE-PSO** shows the disappearance of trimethylsilyl protons and the appearance of vinylene protons (Figure 2, A). Furthermore, the disappearance of vinylene protons and the appearance of epoxy protons are observed in **MTBPSE-PSE** (Figure 2, B). These results revealed that the reaction proceeded according to our expectations.



Scheme 2.

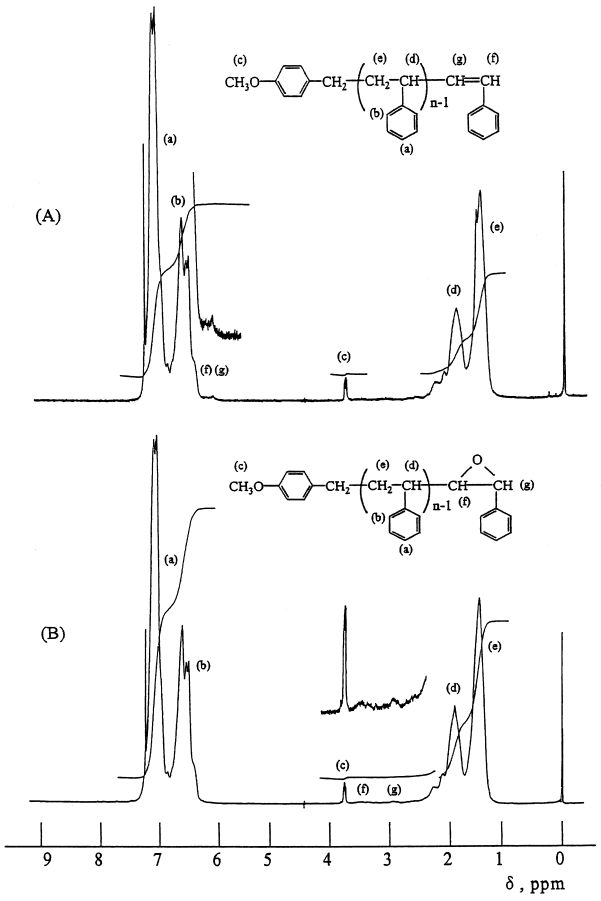
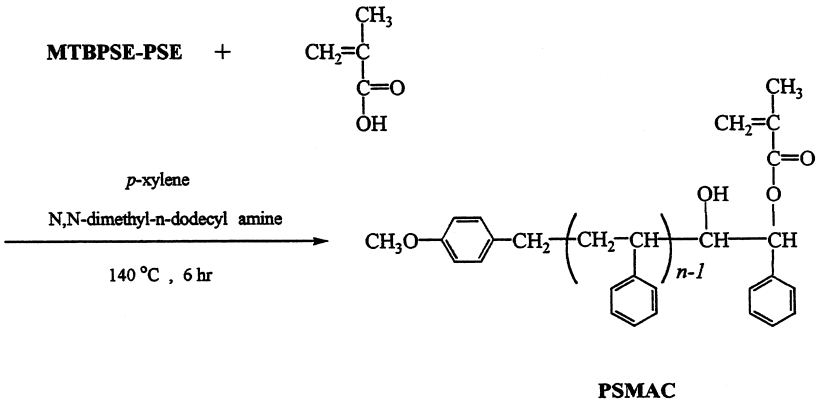


Figure 2. ^{1}H NMR spectrum (400MHz, in $CDCl_3$) of (A) **MTBPSE-PSO** and (B) **MTBPSE-PSE**.



Scheme 3.

Synthesis of Macromonomer

The methacryloyl macromonomer of polystyrene was prepared from **MTBPSE-PSE** with MAA (Scheme 3). Figure 3 shows the ^{1}H-NMR spectrum of the resulting polymer (**PSMAC**, $\overline{M}_n$ = 5,200, $\overline{M}_w/\overline{M}_n$ = 1.36). The signals of

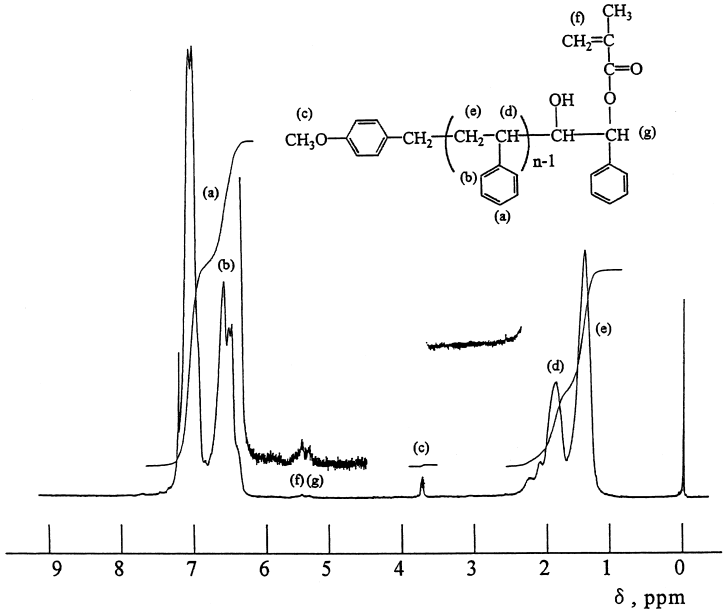


Figure 3. ^{1}H NMR spectrum (400MHz, in $CDCl_3$) of **PSMAC**.

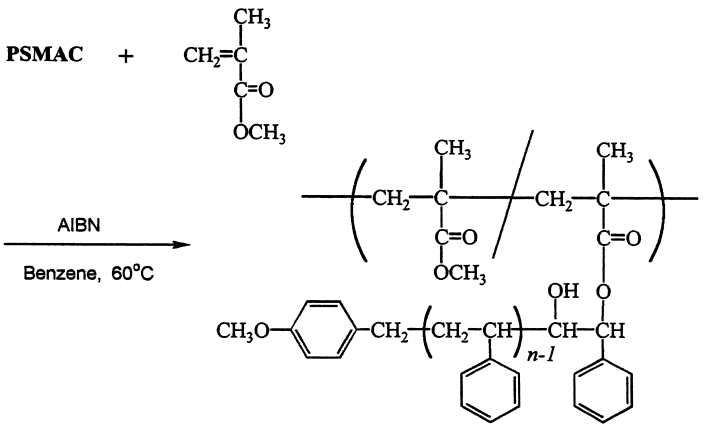
the epoxy group (3.10-3.80 ppm) completely disappeared and new signals assigned to the methacryloyl group appeared (5.30-5.50 ppm).

Homopolymerization

The homopolymerization of **PSMAC** was carried out at 60°C for 1 week using AIBN as the initiator in benzene. The number-average molecular weight was 8,300 ($\overline{M}_w/\overline{M}_n$ = 1.67) for the resulting polymer (**HPSMAC**). In the ^{1}H-NMR spectrum of **HPSMAC**, the signals of vinyl protons at 5.30-5.50 ppm completely disappeared. But, the reason for low reactivity of **PSMAC** is now under investigation.

Graft Copolymerization

The graft copolymerization of **PSMAC** with MMA was carried out at 60°C for 6 hours in benzene (Scheme 4). After polymerization, the resulting polymers were isolated by fractional precipitation using benzene and methanol. These results are shown in Table 1. Residual **PSMAC** was not found in only fraction as confirmed by ^{1}H NMR and GPC, and the yield of graft copolymer increased with increasing the **PSMAC** as macromonomer. GPC curves of the macromonomer and graft copolymer are shown in Figure 4. The curve of graft copolymer showed an unimodal peak. The graft copolymer isolated from the original product obtained shows that the peak due to the styrene macromonomer



PMMA-g-PST

Scheme 4.

TABLE 1. Synthesis of Graft Copolymers

Macromonomer				[M][a]/[MMA]	Benzene	Original Product				Graft Copolymerization[d]		Graft
No.	Feed	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$			Yield[b]	Conversion[c]	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	Homo Poly(MMA)	Graft Copolymer[e]	Copolymer
	(g)			(mol %)	(mL)	(g)	(%)			(Wt %)	(Wt %)	
PSMAC-1	0.100	6,500	1.42	0.082	2	1.76	88.7	29,700	2.39	33.6	66.4	**PMMA-g-PST-1**
PSMAC-2	0.300	6,500	1.42	0.247	2	2.16	99.4	29,600	5.97	26.0	74.0	**PMMA-g-PST-2**
PSMAC-3	0.125	5,200	1.36	0.514	1	0.47	73.7	18,300	4.19	22.5	78.5	**PMMA-g-PST-3**
PSMAC-4	0.175	5,200	1.36	0.719	1	0.49	67.3	17,800	6.37	20.0	80.0	**PMMA-g-PST-4**

[a] [M]=Macromonomer. [b] Yield (g) = Weight of polymer precipitated with Methanol (insoluble part). [c] Conversion (%) = [(Weight of Polymer precipitated - Weight of Macromonomer) / Weight of MMA charged] × 100, that is conversion of MMA. [d] It was carried out using 2 mol % of AIBN for 6 h at 60℃. [e] Extracted with benzene and Methanol.

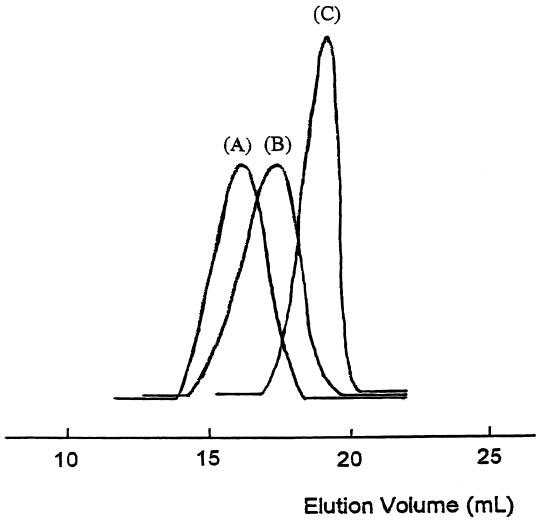


Figure 4. GPC profiles of **PMMA-g-PST-1** ((A), $\overline{M}_n$ = 74,300, $\overline{M}_w/\overline{M}_n$ = 1.87), original product without solvent fractionation ((B), $\overline{M}_n$ = 29,700, $\overline{M}_w/\overline{M}_n$ = 2.39) and polystyrene macromonomer as a prepolymer, **PSMAC-1** ((C), $\overline{M}_n$ = 6,500, $\overline{M}_w/\overline{M}_n$ = 1.42).

is essentially absent. This indicated that the PSMAC worked efficiently as a macromonomer for the preparation of graft copolymer. On the other hand, the numbers of branches of graft copolymer were calculated based on the composition and molecular weight of graft copolymer. They were found to increase with increasing the molecular weight of **PSMAC**. It is summarized in Table 2. From

TABLE 2. The Characterization of Graft Copolymers

No.	Graft Copolymer		
	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	Number of Branches[f]
PMMA-g-PST-1	74,300	1.87	1.0
PMMA-g-PST-2	60,800	1.84	1.8
PMMA-g-PST-3	77,300	1.79	5.0
PMMA-g-PST-4	87,300	2.06	7.5

Calculated based on the composition and the molecular weight of graft copolymer.

the above results, the well-defined graft copolymer can be prepared by the copolymerization of **PSMAC** with MMA.

CONCLUSION

p-Methoxybenzyl *p*-trimethylsilylphenyl selenide works as a photoiniferter, and conducts to end functional polystyrene having phenylseleno group at ω-chain end. The phenylseleno group at ω-chain end in polystyrene was converted to carbon-carbon double bond by hydrogen peroxide. Carbon- carbon double bond was then converted to epoxy group with *m*-chloro-perbenzoic acid. The reaction of polystyrene containing epoxy end group with methacrylic acid afforded well-controlled methacryloyl macromonomer of polystyrene. The copolymerization of this macromonomer with methyl methacrylate effectively yielded a graft copolymer composed of a poly(methyl methacrylate) backbone and polystyrene branches.

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