

SYNTHESIS AND POLYMERIZATION OF α -METHACRYLYOXYL-ETHYLOXYCARBONYLMETHYL- ω -(*N,N*-DIETHYLDITHIOCARBAMYL) POLYSTYRENE MACROMONOMERS

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Abstract Polystyrene macromonomers with different molecular weight were prepared by radical polymerization of styrene (St) in benzene using β -methacryloxyethyl 2-*N,N*-diethyldithiocarbamylacetate (MAEDCA) as a monomer-iniferter. Characterization of the macromonomer by $^1\text{H-NMR}$ showed that the end groups were α -methacryloxyethyl oxycarbonylmethyl and ω -(*N,N*-diethyldithiocarbamyl). The macromonomer was difficult to homopolymerize, but it was easily copolymerized with methyl methacrylate (MMA) initiated by AIBN to form graft copolymers (PMMA-g-PSt) with PSt branches randomly distributed along the PMMA backbone. Copolymerization reaction and the structure of the graft copolymers were strongly affected by M_n and concentration of the macromonomer. The composition and M_n of the purified graft copolymer were determined by $^1\text{H-NMR}$ and GPC analysis.

Key words Monomer-iniferter, Photoiniferter, Macromonomer, Living radical polymerization, Graft copolymer

INTRODUCTION

In recent years, the number of studies on the synthesis and application of macromonomers has rapidly increased because macromonomers are very useful in the synthesis of various kinds of functional graft copolymers having well defined structures^[1-4]. A great number of graft copolymers, such as hard/soft^[5], crystalline/noncrystalline, hydrophilic/hydrophobic, and polar/non-polar^[6] graft copolymers, were successfully prepared by the copolymerization of macromonomers. In addition, macromonomers have some advantages such as non-volatility and high solubility over those of small monomers and polymers, which make it easy to carry out further reaction. Therefore, it is important work to design and synthesize macromonomers with various structures.

Macromonomers are generally synthesized by living ionic polymerizations by one of two methods^[1, 7-9]. The first is called the initiation method, which involves the initiation of vinyl monomer with a initiator containing a polymerisable group which is not affected by the polymerization. The second is called the end-capping method which involves the end capping of either living anionic polymers with a polymerisable electrophile, or living cationic polymers with a nucleophile containing a polymerisable group. Other methods for the synthesis of macromonomers are group-transfer polymerization, step-growth process, and transformation of ω -functionalized polymers^[7, 8]. Concerning the synthesis of macromonomers via conventional radical polymerization, some other methods such as chain transfer polymerization^[10-13] and introduction of the unsaturation group to macromonomer precursors^[12, 14-16] were also reported. Recently, "living"/controlled radical polymerization methods were introduced into macromonomer synthesis, Matyjaszewski and coworkers^[17, 18] used allyl chloride-CuCl-2,2'-bipyridine (bpy) and vinyl chloroacetate-CuCl-bpy initiating system via an atom transfer radical polymerization (ATRP) process to synthesize α -allyl- ω -chloro-polystyrene and α -vinyl oxycarbonylmethyl- ω -chloro-polystyrene, respectively. Otsu and coworkers^[19] also reported the use of an iniferter, such as 4-vinylbenzyl *N,N*-diethyldithio-

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Received January 10, 2000

carbamate for the preparation of macromonomer.

In this article, we describe the synthesis and characterization of α -methacryloxyethyloxycarbonylmethyl- ω -(*N,N*-diethyldithiocarbamyl)polystyrene macromonomers by radical polymerization of St initiated with β -methacryloxyethyl 2-*N,N*-diethyldithiocarbamylacetate, and the copolymerization behavior of this macromonomer.

EXPERIMENTAL

Materials

Methyl methacrylate and styrene were freshly distilled before use. β -Methacryloxyethyl 2-*N,N*-diethyldithiocarbamylacetate (MAEDCA) was synthesized by the reaction of 2-methacryloxyethyl chloroacetate with sodium diethyldithiocarbamate as reported previously^[20]. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Solvent and other reagents were used after purification by ordinary methods.

Synthesis of PSt-Macromonomer

Photopolymerizations of St in benzene initiated with MAEDCA monomer-iniferter were carried out in sealed glass tubes at ambient temperature under UV light irradiation with a 250 W UV lamp at a distance of 20 cm. After polymerization for a given time, the contents of the tubes were dissolved in tetrahydrofuran (THF), then poured into a large amount of methanol, and the conversion was calculated from the weight of the PSt-macromonomer. The PSt-macromonomer was further purified by threefold reprecipitation from a benzene solution with methanol as the precipitant.

Copolymerization of PSt-Macromonomers with MMA

Copolymerizations of PSt-macromonomers with MMA in different feeds using AIBN as initiator were carried out in benzene at 65°C. The resultant polymers were precipitated with a large amount of methanol. The copolymers were purified by solution extraction with suitable solvents, PMMA homopolymer with 95% ethanol, and the remaining PSt-macromonomer with cyclohexane.

Characterization

Molecular weight and molecular weight distribution data of the polymers were determined by gel permeation chromatography (GPC) using THF as the eluent with a flow rate of 1.0 mL/min at 35°C through three Waters μ -Styragel columns (HT2+HT3+HT4) in series and a Waters 515 RI detector. The column system was calibrated by a set of standard monodisperse polystyrenes. The data analysis was accomplished on a Waters Millennium 32 system. IR and ¹H-NMR spectra were recorded on a Nicolet IR 750 spectrometer and on a Bruker ARX 400 spectrometer, respectively. The number of the *N,N*-diethyldithiocarbamate (Et₂NCSS) end groups of PSt-macromonomer was determined in THF by UV spectroscopy using a Shimadzu UV-250 instrument (MAEDCA as standard, at 278.9 nm). The glass transition temperature (*T*_g) was determined with a TA DSC-2010 differential scanning calorimeter at a heating rate of 10 K/min.

RESULTS AND DISCUSSION

Syntheses and Characterization of PSt-Macromonomer

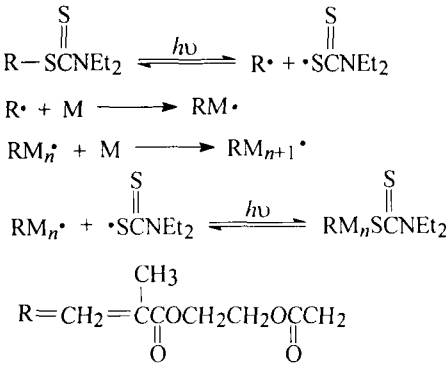
Polymerizations of St in the presence of the monomer-iniferter MAEDCA were carried out in benzene at ambient temperature under UV light irradiation. Table I shows the data obtained from the polymerization at different time intervals, from which it can be seen that the conversion and *M*_n of the resulting PSt-macromonomers increase with increasing time. Furthermore, the number of Et₂NCSS end group of PSt-macromonomers is almost the same and around 1.0, indicating that Et₂NCSS· reacts with the growing radical efficiently. These results reveal that the polymerization proceeds through a "living" radical polymerization mechanism as shown in Scheme 1. We have investigated the photodissociation of MAEDCA and PSt-macromonomer^[21], and found that the "living" polymerization behavior was similar to the polymerization using other iniferter containing *N,N*-diethyldithiocarbamyl group as reported previously^[22, 23]. In addition, we also found that when the conversion of

St monomer was greater than 50%, the methacryl end group of the resultant PSt-macromonomer could partly participate in polymerization. In this case, the values of M_n and M_w/M_n data increased remarkably, and the number of Et₂NCSS end group was much greater than 1.

Table 1. Polymerization of St with MAEDCA monomer-iniferter under UV light irradiation at ambient temperature^a

Samples	Time (h)	M_n (10 ⁻³)	M_w/M_n	Conversion (%)	Number of End Group (Et ₂ NCSS)
1	1.0	2.7	1.63	10.8	1.04
2	2.0	4.5	1.72	16.0	1.00
3	3.0	6.2	1.79	22.0	0.99
4	4.0	9.7	1.81	31.7	1.02
5	5.0	12.1	1.84	41.7	0.97
6	6.0	14.3	1.97	48.2	1.11

^a Polymerization condition: [St] = 7.0 mol/L, [MAEDCA] = 2.0 × 10⁻² mol/L, in benzene



Scheme 1

We have studied the effect of MAEDCA concentrations on the polymerization of St and the data are compiled in Table 2. They show that the molecular weights of the resulting PSt-macromonomers decrease with increasing MAEDCA concentrations. The effect of St concentration on polymerization is shown in Fig. 1, from which we can see that the molecular weights of PSt-macromonomers increase with increasing St concentrations, and the molecular weight distributions (MWD) are essentially the same at around 1.50. Therefore, the molecular weights of the PSt-macromonomers can be determined by St conversion and the molar ratio of St and MAEDCA.

Table 2. Effect of MAEDCA concentration on M_n of PSt-macromonomer^a

Samples	[MAEDCA] (10 ² mol/L)	M_n (10 ⁻³)	M_w/M_n	Conversion (%)	Number of End Group (Et ₂ NCSS)
1	1.4	4.1	1.60	6.11	1.02
2	3.5	3.6	1.53	8.24	0.99
3	4.7	3.2	1.47	8.78	1.01
4	6.4	2.8	1.46	10.05	1.00
5	7.2	2.5	1.44	11.22	0.97
6	8.0	2.4	1.46	12.45	1.02
7	8.7	2.2	1.42	13.31	0.98

^a Polymerization condition: [St] = 5.0 mol/L, time = 1 h, under UV light irradiation at ambient temperature, in benzene

The end groups of PSt-macromonomer prepared were characterized by ¹H-NMR, IR and UV spectroscopies. In the ¹H-NMR spectrum of PSt-macromonomer, the chemical shifts δ assigned to the corresponding protons are as follows: 1.20 and 1.28 [SSCN(CH₂CH₃)₂], 1.94 [CH₂=C(CH₃)], 3.62 and 3.90 [SSCN(CH₂-CH₃)₂], 2.05[OC(O)CH₂-], 4.12~4.22 [- (O)COCH₂CH₂OC(O)-], 5.57 (CH=) and 6.10 shifts of the repeat

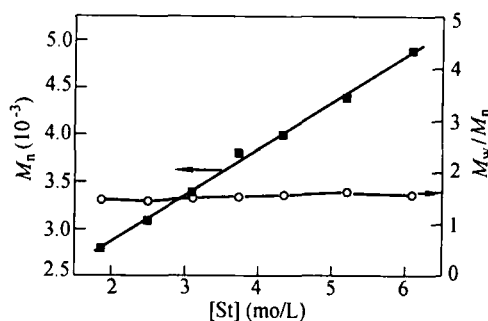
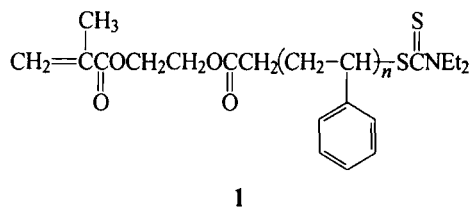


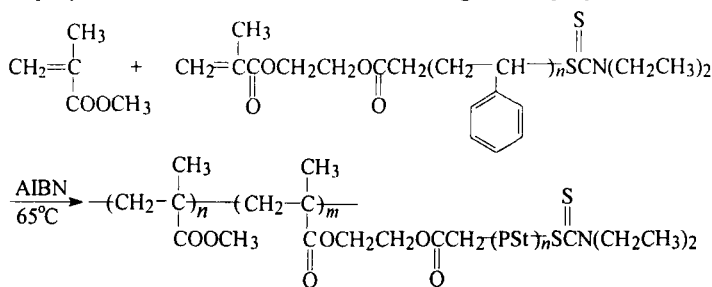
Fig. 1 Effect of St concentration on M_n of PSt-macromonomer
[MAEDCA] = 2.49×10^{-2} mol/L, time = 1 h

units of St, i.e., 6.25~7.32 [C_6H_5-] and 1.21~2.38 [$-\text{CH}_2\text{CH}-$]. The IR spectrum of PSt-macromonomer has the characteristic absorptions of carbon-carbon double bond at 1637 cm^{-1} and thio-carbonyl group at 1269 cm^{-1} . In the UV spectrum, the characteristic absorption at 278.9 nm corresponds to the $(\text{C}_2\text{H}_5)_2\text{NCSS}$ group, and the number of the $(\text{C}_2\text{H}_5)_2\text{NCSS}$ group in PSt-macromonomer was about 1.0, as summarized in Tables 1 and 2. All the above results indicate that the end groups of PSt-macromonomer contain an α -methacryloxyethyloxycarbonylmethyl group and an ω -(*N,N*-diethyldithiocarbamyl) group, which are consistent with the structure of PSt-macromonomer 1:



Polymerization of PSt-Macromonomer

When the homopolymerization of PSt-macromonomer initiated by AIBN was carried out in benzene at 65°C , it was quite difficult to implement and only a small amount of homopolymerization product of PSt-macromonomer was obtained even after 60 h. This might be due to the low reactivity of the macromonomer. However, PSt-macromonomer can easily copolymerize with MMA to form PMMA-*g*-PSt copolymers as shown in Scheme 2.



Scheme 2

We investigated the copolymerization of PSt-macromonomer with MMA at 65°C using AIBN as an initiator. After 24 h, the obtained polymer was extracted with hot cyclohexane to remove the remaining PSt-macromonomer and with 95% ethanol to remove PMMA homopolymer. The copolymerization data for macromonomers with different molecular weights are compiled in Table 3, from which we can see that the effect of the molecular weight of macromonomer on copolymerization is remarkable, the conversion of MMA and the M_n values of copolymers decreased with increasing molecular weight of macromonomer. This result is ascribed

to the reactivity of macromonomer which decreases with increasing chain length (molecular weight). The copolymerization was further examined at higher macromonomer contents in the feed, and the results are shown in Fig. 2. The M_n values of copolymer decrease significantly with increasing in macromonomer content of the feed below 10 mol%, after that M_n is almost unaffected by the macromonomer content.

Table 3. Effect of molecular weight of PSt-macromonomer ($M_{n, M1}$) on the copolymerization reaction in benzene at 65°C^a

Samples	$M_{n, M1}^b$ (10^{-3})	C_2^c (%)	C_1^d (%)	M_n of Copolymer (10^{-3})	M_w/M_n	N_g
1	2.7	74.5	73.6	98.5	1.98	6.6
2	4.5	72.3	70.2	85.6	2.07	5.5
3	6.2	68.5	66.5	76.4	2.01	4.5
4	9.7	63.6	61.0	67.9	1.95	3.0
5	12.1	58.7	53.4	55.8	2.03	2.3
6	14.3	55.5	49.0	45.6	2.07	1.6

^a Polymerization condition: [PSt-macromonomer] = 7.5×10^{-3} mol/L, [MMA] = 3.2 mol/L, [AIBN] = 2×10^{-3} mol/L, and time = 24 h

^b $M_{n, M1}$: Number-average molecular weight of PSt-macromonomer determined by GPC

^c C_2 : Conversion of MMA

^d C_1 : Conversion of PSt-macromonomer

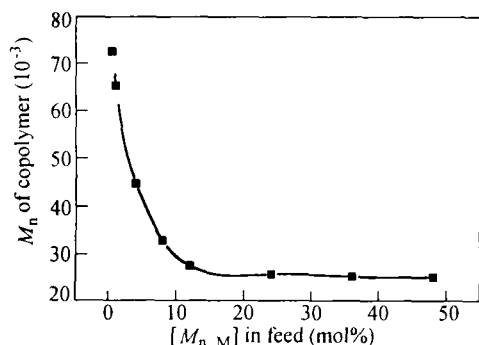


Fig. 2 Dependence of M_n of graft copolymer on PSt-macromonomer with $M_n = 3,600$ in feed; [MMA] = 3.2 mol/L, [AIBN] = 2×10^{-3} mol/L, and time = 24 h

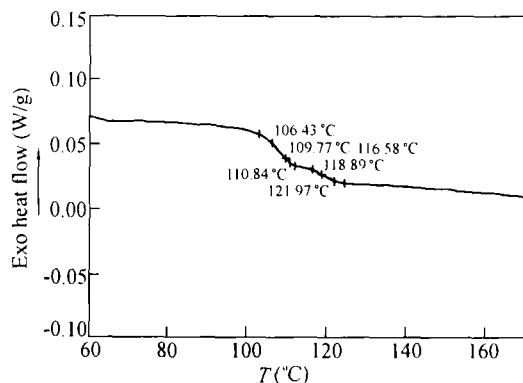


Fig. 3 DSC curves of PMMA-g-PSt copolymers

Characterization of Graft Copolymer

The composition and M_n of the purified graft copolymer were determined by $^1\text{H-NMR}$ and GPC analysis, respectively. The average side chain number (N_g) of the graft copolymer was calculated from the equation: $N_g = M_n W_g / M_{M1}$, where M_n is the molecular weight of graft copolymer, W_g is the weight percent of PSt-macromonomer in copolymer and M_{M1} is molecular weight of PSt-macromonomer. The decrease of N_g data with increasing molecular weight of PSt-macromonomer is seen in Table 3, indicating that the reactivity of the PSt-macromonomer decreases with increasing molecular weight. Characterization results show that the contents of PSt with molecular weights $2.7\sim 14.3 \times 10^3$ as chain branches in the copolymers are from 18.1% to 50.2% by weight and the average number of branches per molecule is 1.6~6.6.

The structure of the obtained graft copolymer was also elucidated by IR and DSC spectroscopies. The IR spectrum of PMMA-g-PSt has the characteristic adsorption peaks of PMMA at 1731 cm^{-1} ($\nu_{\text{C=O}}$), 1150 cm^{-1} ($\nu_{\text{C-O-C}}$) and PSt at 700 cm^{-1} , 1600 cm^{-1} and 3082 cm^{-1} (ν_{phenyl}), respectively. The DSC curve of PMMA-g-PSt is shown in Fig. 3, in which two glass transition temperatures T_g at 118.9 and 109.8°C can be seen clearly. In a comparison experiment the T_g values of PMMA and PSt were determined to be 126 and 83°C, respectively. This

confirms that the graft copolymer is successfully obtained.

CONCLUSIONS

Poly(styrene) macromonomers with different molecular weights were prepared by radical polymerization of styrene (St) with β -methacryloxyethyl 2-*N,N*-diethyldithiocarbamyl-acetate (MAEDCA) as a monomer-iniferter. The molecular weights of the PSt-macromonomers can be determined from St conversion and the molar ratio of St and MAEDCA. The macromonomer was easily copolymerized with methyl methacrylate in the presence of AIBN to form graft copolymers (PMMA-*g*-PSt) with PSt branches randomly distributed along the PMMA backbone. Copolymerization reaction and structure of the graft copolymers were strongly affected by M_n and the concentration of macromonomer. The composition and M_n of the purified graft copolymer were determined by $^1\text{H-NMR}$ and GPC analysis. The results show that the contents of PSt with molecular weights $2.7\sim 14.3 \times 10^3$ as chain branches in the copolymers are from 18.1% to 50.2% by weight and the average number of branches per molecule is 1.6–6.6.

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