

Synthesis of Macromonomer from Radical Polymerization of Styrene with a Polymerizable Photoiniferter

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ABSTRACT: α -(Methacryloxyethyloxycarbonylmethyl)- ω -(*N,N*-diethyldithiocarbamyl)-polystyrene macromonomers with different molecular weights were prepared by radical polymerization of styrene (St) using β -methacryloxyethyl 2-*N,N*-diethyldithiocarbamylacetate (MAEDCA) as a polymerizable photoiniferter in toluene under ultraviolet light. The polymerization of St with MAEDCA carried out by a "living" process; that is, both the yield and the molecular weight of the resultant polymers increased with increasing of reaction time, and the resultant polymer was a macromonomer, for example, α -(methacryloxyethyloxycarbonylmethyl)- ω -(*N,N*-diethyldithiocarbamyl)-polystyrene, designated as PSt-macromonomer. The molecular weight of the PSt-macromonomer depended on the concentrations of the polymerizable photoiniferter and St, as well as the conversion of St. The PSt-macromonomer can copolymerize with MMA initiated by AIBN at 65°C to form a graft copolymer (PMMA-*graft*-PSt) with PSt branches randomly distributed along the PMMA backbone. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1350–1356, 2000

Key words: β -methacryloxyethyl 2-*N,N*-diethyldithiocarbamylacetate; photoiniferter; PSt-macromonomer; graft copolymer

INTRODUCTION

Macromonomers, as a kind of macromolecules with polymerizable functional groups, have been widely used in the molecular design of polymers because of their importance role in the synthesis of functional copolymers.^{1–4} Various kinds of graft copolymers with uniform graft chain and different structure and properties were prepared by them. Hard/soft,⁵ crystalline/noncrystalline, hydrophilic/hydrophobic, and polar/inpolar⁶ graft copolymers were successfully prepared, which overcame the shortcoming of inhomogeneity of graft chains obtained by common methods.⁷ Therefore, polymer scientists pay great attention to the synthesis and polymerization of macromonomers, which has been taken as an independent research field called macromolecule technology.⁷

The synthesis of macromonomers are generally carried out by ionic polymerizations, group-transfer polymerization, step-growth process or from transformation of ω -functionalized polymers.^{8,9} Although there are some methods for synthesis of macromonomers via conventional radical polymerization, such as by the chain transfer polymerization method^{10–13} or by synthesis of macromonomer precursors, then introduction the unsaturation method,^{2,14–16} the synthesis of macromonomers via radical polymerization by one step using the initiator-bearing vinyl group are rarely reported. Recently, Matyjaszewski and coworkers^{17,18} reported the synthesis of well-defined polymers, that is, α -allyl- ω -chloropolystyrene and α -vinylloxycarbonylmethyl- ω -chloropolystyrene from an atom transfer radical poly-

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merization (ATRP) of styrene using an allylchloride-CuCl-bipyridine and vinyl chloroacetate-CuCl-bipyridine initiating system, respectively. Otsu and coworkers¹⁹ reported that the iniferter, such as 4-vinylbenzyl *N,N*-diethyldithiocarbamate, could be used for the preparation of macromonomer-iniferter and the synthesis of graft and crosslinked polymers.

In this article, we would like to report some results on the synthesis and characterization of a macromonomer, α -(methacryloxyethyloxycarbonylmethyl)- ω -(*N,N*-diethyldithiocarbamyl)-polystyrene, designated as PSt-macromonomer, by the polymerization of styrene in the presence of a polymerizable photoiniferter, such as β -methacryloxyethyl 2-*N,N*-diethyldithiocarbamylacetate (MAEDCA), in toluene under ultraviolet (UV) light irradiation. The mechanism of polymerization is proposed based on radical trapping and the electron paramagnetic resonance (EPR) studies. The formation of graft copolymer PMMA-*graft*-PSt from copolymerization of PSt-macromonomer with MMA is also discussed.

EXPERIMENTAL

Materials

β -Methacryloxyethyl 2-*N,N*-diethyldithiocarbamylacetate was synthesized by the method reported previously.²⁰ 2-Methyl-2-nitrosopropane (MNP) was purchased from the Aldrich Chemical Company. Methyl methacrylate and styrene monomers, organic solvents, and other reagents were used after ordinary purifications.

Synthesis of PSt-Macromonomers

Photopolymerizations of St in toluene with MAEDCA as iniferter were carried out in sealed

glass tubes at ambient temperature under 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 poured into a large amount of methanol, and the conversion was calculated from the weight of the resultant PSt-macromonomer. The PSt-macromonomer was further purified by a reprecipitation method from a benzene solution with methanol as precipitant three times.

Copolymerization of PSt-Macromonomers

Copolymerizations of PSt-macromonomer with MMA were carried out in glass tubes. Graft copolymerization of PSt-macromonomer with MMA initiated by AIBN was carried out in benzene at 65°C. After polymerization for a certain time, the resultant polymer was precipitated with a large amount of methanol. The resultant polymers were further purified by extraction with suitable solvents, PMMA homopolymer with 95% ethanol, and PSt-macromonomer with cyclohexane, and the residual product is PMMA-*graft*-PSt.

Characterization

Molecular weights and molecular weight distributions of PSt-macromonomers and copolymers were determined by gel permeation chromatography (GPC) on a Waters 2410 instrument using tetrahydrofuran (THF) as eluent and calibration with polystyrene standards. The number of the *N,N*-diethyldithiocarbamate (Et₂NCSS) end groups of PSt-macromonomer in THF was determined by UV spectroscopy recorded on a Shimadzu UV-250 instrument (MAEDCA as standard, at 278.5 nm). Infrared (IR) and ¹H nuclear magnetic resonance (¹H-NMR) spectra were recorded on a Nicolet IR 750 spectrometer and on a Bruker ARX 400 spec-

Table I Effect of St Concentration on M_n in the Photopolymerization of St Using MAEDCA Iniferter 20°C in Toluene

| Samples | [St] (mol L ⁻¹) | M_n (10 ⁻³) | M_w/M_n | Conversion (%) | Numbers of End Group (Et ₂ NCSS) |
|---------|--------------------------------|------------------------------|-----------|-------------------|--|
| 1 | 1.86 | 2.8 | 1.48 | 5.73 | 1.02 |
| 2 | 2.49 | 3.1 | 1.45 | 6.24 | 0.99 |
| 3 | 3.11 | 3.4 | 1.51 | 7.62 | 1.01 |
| 4 | 3.73 | 3.8 | 1.53 | 8.55 | 1.00 |
| 5 | 4.35 | 4.0 | 1.56 | 9.94 | 0.97 |
| 6 | 5.20 | 4.4 | 1.59 | 10.61 | 1.02 |
| 7 | 6.09 | 4.9 | 1.57 | 12.13 | 0.98 |

Polymerization condition: [MAEDCA] = 2.49×10^{-2} mol L⁻¹; t = 1 h.

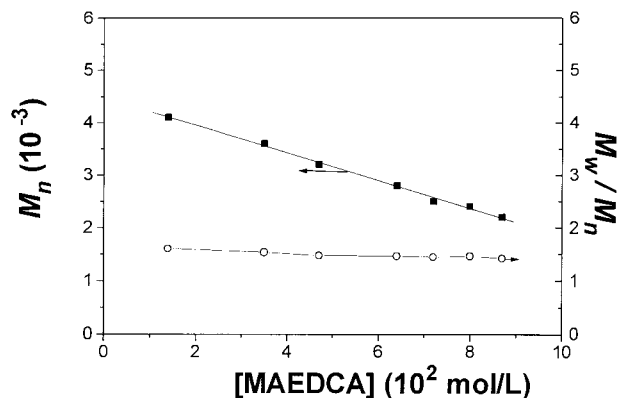


Figure 1 Effect of MAEDCA concentration on M_n of PSt-macromonomer; $[St] = 5.0 \text{ mol L}^{-1}$; $t = 1 \text{ h}$.

trometer using CDCl_3 as the solvent and tetramethylsilane as the internal reference, respectively. EPR spectra were recorded on a Bruker ER 200D-SRC electron spin resonance spectrometer using the TM cavity at the X-band in a quartz EPR tube with 100 kHz modulation and 1.00 mW microwave power, with MNP used as the spin trapping agent. The glass transition temperature (T_g) was determined with a TA DSC-2010 differential scanning calorimeter at a heating rate of 10°C min .

RESULTS AND DISCUSSION

Polymerization of St in the Presence of a Polymerizable Photoiniferter MAEDCA

Polymerization of St in the presence of a polymerizable photoiniferter MAEDCA was carried out in toluene at 20°C under UV light irradiation. The results of the photopolymerization using various concentrations of St are compiled in Table I. It

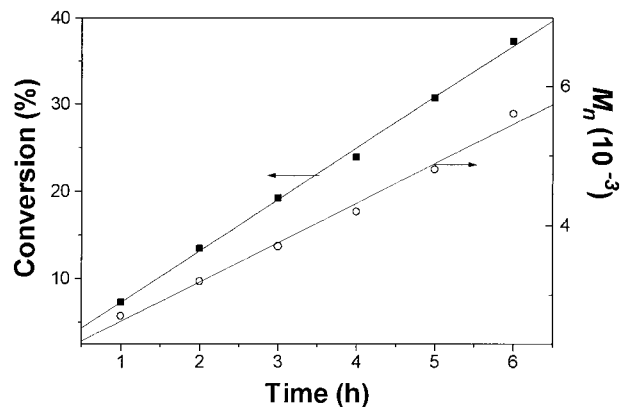


Figure 2 Time-conversion and time- M_n relations for solution polymerization of St with MAEDCA at 20°C ; $[St] = 5.0 \text{ mol L}^{-1}$; $[MAEDCA] = 5.0 \times 10^{-2} \text{ mol L}^{-1}$.

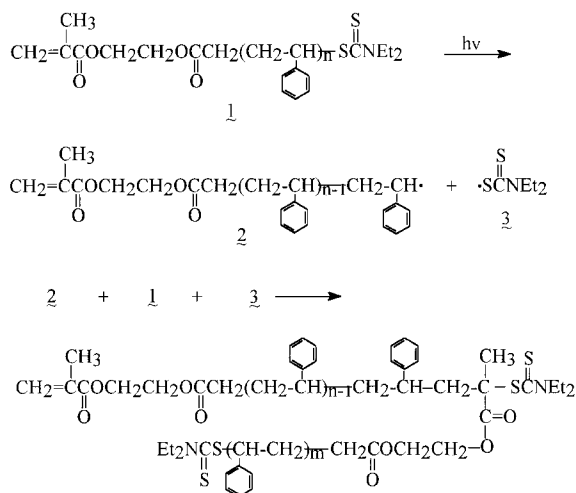
shows that the molecular weights linearly increase with St concentrations. The effect of MAEDCA concentration on the St polymerization is shown in Figure 1, from which we can see that the molecular weights of PSt-macromonomer decrease with the increasing of MAEDCA concentrations. Therefore, the molecular weight of PSt-macromonomer can be controlled by MAEDCA and St concentrations, while the molecular weight distributions (MWD) are the same, at around 1.50.

When the solution polymerization was carried out at different times, the data are compiled in Table II. It can be seen that the conversion and M_n of PSt-macromonomers are linearly increased with the increasing of time, respectively (Fig. 2), while the values of M_w/M_n increase with reaction time from 1.45 for 1 h to 2.36 for 6 h. However, the numbers of Et_2NCSS end group of PSt-macromonomers are almost the same around 1.0. The results indicate that the polymerization exhibits

Table II Polymerization of St with Polymerizable Photoiniferter MAEDCA at Different Reaction Times at 20°C in Toluene

| Samples | Time (h) | M_n (10^{-3}) | M_w/M_n | Conversion (%) | Numbers of End Group (Et_2NCSS) |
|---------|----------|---------------------|-----------|----------------|---|
| 1 | 1.0 | 2.7 | 1.45 | 7.28 | 0.98 |
| 2 | 2.0 | 3.2 | 1.52 | 13.44 | 1.00 |
| 3 | 3.0 | 3.7 | 1.98 | 19.22 | 1.02 |
| 4 | 4.0 | 4.2 | 2.01 | 23.83 | 0.99 |
| 5 | 5.0 | 4.9 | 2.09 | 30.67 | 1.05 |
| 6 | 6.0 | 5.6 | 2.36 | 37.22 | 1.09 |

Polymerization condition: $[St] = 5.0 \text{ mol L}^{-1}$; $[MAEDCA] = 5.0 \times 10^{-2} \text{ mol L}^{-1}$.



Scheme 1

some characteristics of “living” radical polymerization, as reported in the literature^{21–25} using monofunctional iniferter containing *N,N*-diethyldithiocarbamyl group. 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 polymerization, as shown in Scheme 1.

In this case, the values of M_n and M_w/M_n data increased remarkably, and the number of Et_2NCSS end groups was much greater than 1 (e.g., when conversion = 53%; $M_n = 12,800$,

$M_w/M_n = 5.13$, and the number of Et_2NCSS end groups = 1.63 was observed).

The end groups of PSt-macromonomer prepared were confirmed by $^1\text{H-NMR}$, IR, and UV spectroscopies. In the $^1\text{H-NMR}$ spectrum of PSt-macromonomer, as shown in Figure 3, the chemical shifts δ (ppm) and assign to the corresponding protons are as follows: 1.20 and 1.28 [$\text{SSCN}(\text{CH}_2\text{CH}_3)_2$], 1.94 [$\text{CH}_2=\text{C}(\text{CH}_3)$], 3.62 and 3.90 [$\text{SSCN}(\text{CH}_2\text{CH}_3)_2$], 2.05 [$\text{OC}(\text{O})\text{CH}_2-$], 4.12–4.22 [$-(\text{O})\text{COCH}_2\text{CH}_2\text{OC}(\text{O})-$], 5.57 and 6.10 ($\text{CH}_2=$), and the characteristic chemical shifts of the repeat units of St, that is, 6.25–7.32 [C_6H_5-] and 1.21–2.38 [$-\text{CH}_2\text{CH}-$]. In addition, the δ at 7.32 ppm is the peak of CDCl_3 solvent. The IR spectrum of PSt-macromonomer has the characteristic absorptions of carbon—carbon double bond at 1637 cm^{-1} and the thiocarbonyl group at 1269 cm^{-1} . In UV spectrum, the characteristic absorption at 278.5 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 a unit, as summarized in Tables I and II. All these indicate that the end groups of PSt-macromonomer contain an α -(methacryloxyethyl)oxycarbonylmethyl group and an ω -(*N,N*-diethyldithiocarbamyl) group, which are consistent with the structure of PSt-macromonomer 1, as follows:

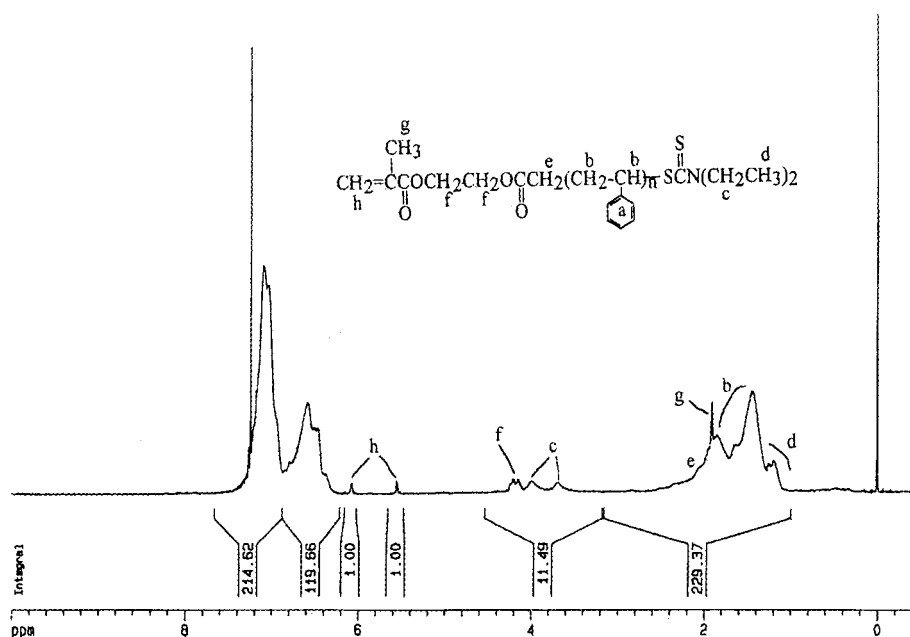
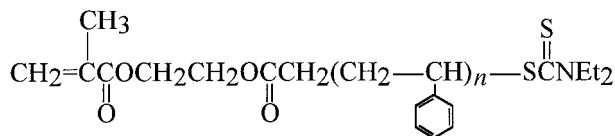


Figure 3 $^1\text{H-NMR}$ spectrum of PSt-macromonomer with $M_n = 3100$; $M_w/M_n = 1.45$.

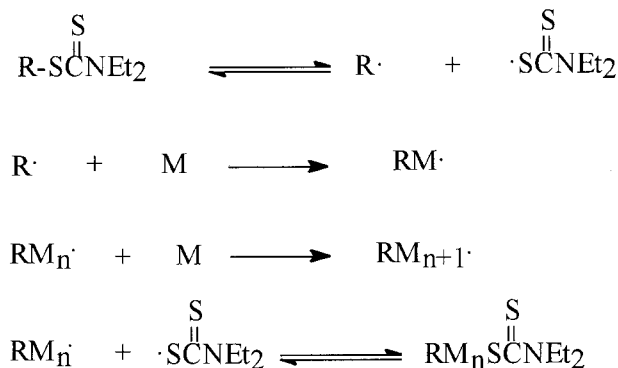


Initiation Mechanism of Photopolymerization and EPR Studies

The mechanism of St polymerization with iniferters having the *N,N*-diethyldithiocarbamyl (DC) group was proposed by Otsu and coworkers,²⁶ as shown in Scheme 2.

The iniferter photochemically dissociates into a carbon-centered radical R^\bullet and a sulfur-centered radical $\text{Et}_2\text{NCSS}^\bullet$. The R^\bullet radical is reactive and will initiate monomer polymerization, and the $\text{Et}_2\text{NCSS}^\bullet$ radical with low reactivity that reacted mainly with growing radicals RM_n^\bullet to form a dormant covalent species, which can further dissociate photochemically. Van Kerckhoven²⁷ also confirmed that photochemical cleavage of the $\text{R}_2\text{NCSS}-\text{C}$ bond might provide a reversible system.

In order to identify the polymerization mechanism, it was important to clarify the photodissociation of MAEDCA and PSt-macromonomer **1**. The radical intermediates of the reaction were investigated by spin-trapping and the EPR technique. The EPR spectrum of MAEDCA/MNP (2-methyl-2-nitrosopropane) system was recorded under UV light irradiation and is shown in Figure 4, from which a mixture of two nitroxy radicals from spin adducts with MNP can be observed. Radical **6** with the hyperfine splitting constants $\alpha_\alpha^N = 14.0$ G, $\alpha_\beta^H = 7.5$ G is formed from the addition of a primary carbon centered radical **4** with the MNP. It is similar to the (ethyl *N,N*-diethyldithiocarbamylacetate)/MNP (EDCA/MNP)



Scheme 2

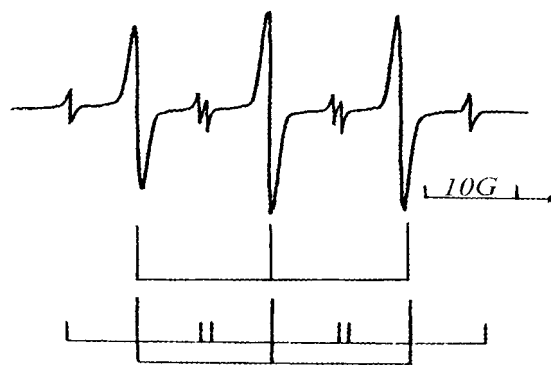
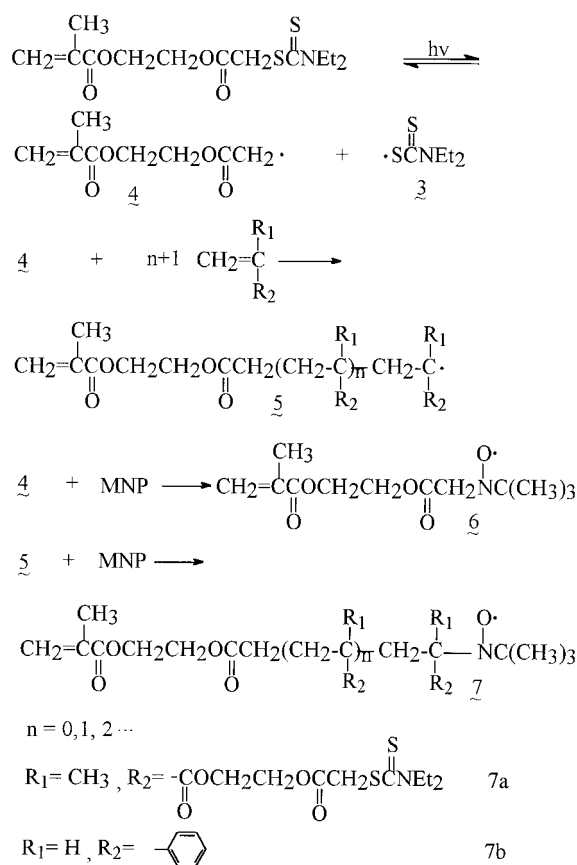


Figure 4 EPR spectrum of MAEDCA-MNP system obtained under UV light irradiation at ambient temperature: $1 \text{ mT} = 10 \text{ G}$; $[\text{MAEDCA}] = 0.20 \text{ mol L}^{-1}$; $[\text{MNP}] = 0.02 \text{ mol L}^{-1}$.

system in which the hyperfine splitting constants of nitroxy radical from the addition of a primary carbon-centered radical (ethoxycarbonylmethyl radical) with the MNP are $\alpha_\alpha^N = 14.1$ G, $\alpha_\beta^H = 7.5$ G²³; radical **7a** with hyperfine splitting constant $\alpha_\alpha^N = 14.1$ G is contributed to the addition of



Scheme 3

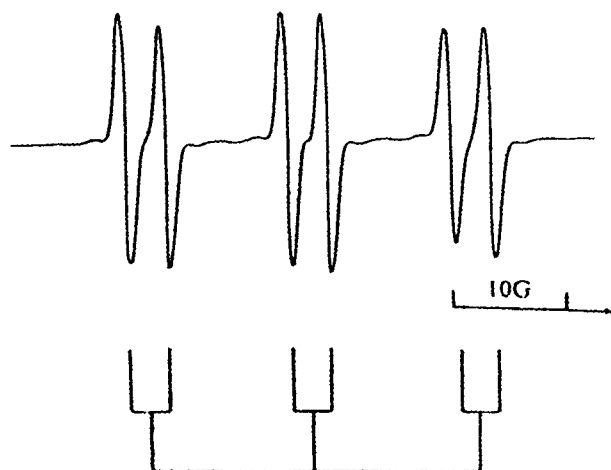
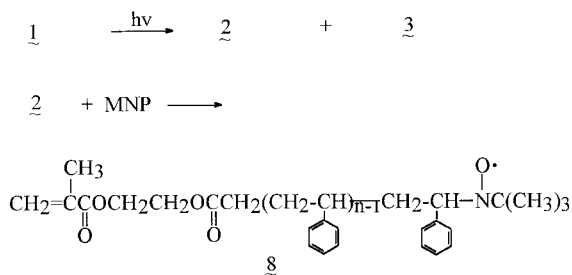


Figure 5 EPR spectrum of MAEDCA-St-MNP system obtained under UV light irradiation at ambient temperature: [MAEDCA] = 0.05 mol L⁻¹; [St] = 8.0 mol L⁻¹; [MNP] = 0.02 mol L⁻¹.

MNP with a tertiary carbon centered radical **5**, which is formed from the addition of radical **4** with the double bond of MAEDCA, as shown in Scheme 3.

In addition, the EPR spectrum of St/MAEDCA/MNP system under irradiation by UV light is shown in Figure 5, from which only the signal of radical **7b** ($\alpha_{\alpha}^N = 14.1$ G; $\alpha_{\beta}^H = 3.6$ G) was found. Figure 6 shows the EPR spectrum of the PSt-macromonomer/MNP system under UV irradiation. The spectrum is assigned to a radical **8** with the hyperfine splitting constant $\alpha_{\alpha}^N = 14.2$ G and $\alpha_{\beta}^H = 3.6$ G, which is formed from the reaction of MNP with **2**, as shown in Scheme 4.

The EPR studies, as mentioned above, indicated that the dissociation reaction of C—S bond under UV light was reversible and confirmed that the mechanism of St polymerization with MAEDCA as photoiniferter proceeds via the reversible dissociation reaction of C—S bonds of dormant species under UV light irradiation.



Scheme 4

Copolymerization of PSt-Macromonomer with MMA

The copolymerization of PSt-macromonomer with MMA was carried out in benzene using AIBN as an initiator at 65°C. The resultant graft copolymers (PMMA-graft-PSt) were obtained. The graft copolymer was confirmed by IR and DSC spectroscopies. The IR spectrum of PMMA-graft-PSt has the characteristic adsorption peaks of PSt at 698, 1601, and 3082 cm⁻¹ ($\nu_{\text{C}_6\text{H}_5}$) and PMMA at 1731 cm⁻¹ ($\nu_{\text{C}=\text{O}}$) and 1150 cm⁻¹ ($\nu_{\text{C}-\text{O}-\text{C}}$), respectively. The DSC curve of PMMA-graft-PSt shows two glass transition temperatures at 107 and 116°C. In a comparison experiment, the T_g values of PS and PMMA were determined to be 97 and 125°C, respectively. In addition, M_n of the graft copolymer ($M_n = 25,200$) was larger than that of the original PSt-macromonomer ($M_n = 3,200$). This research work is progressing, and the detailed results will be published in another article.

CONCLUSIONS

Our results indicate that PSt-macromonomer can be prepared by “living” radical polymerization of styrene (St) with β -methacryloxyethyl 2-*N,N*-diethylthiocarbamylacetate, a polymerizable photoiniferter, in toluene under UV light irradiation. The molecular weight of the PSt-macromonomer depended on the concentrations of the polymeriz-

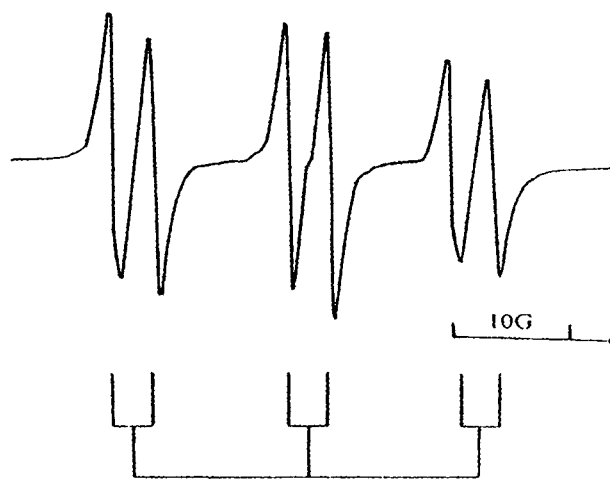


Figure 6 EPR spectrum of PSt-macromonomer-MNP system obtained under UV light irradiation at ambient temperature: [PSt-macromonomer] = 0.10 g mL⁻¹; [MNP] = 0.02 mol L⁻¹.

able photoiniferter and St, as well as the conversion of St. The resultant PSt-macromonomer can polymerize with MMA initiated by AIBN at 65°C to form graft copolymer (PMMA-*graft*-PSt) with PSt branches randomly distributed along the PMMA backbone.

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