A Novel Strategy To Synthesize Graft Copolymers with Controlled Branch Spacing Length and Defined Grafting Sites

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ABSTRACT: We report a novel method to prepare graft copolymers (PS-*g*-PEGM and PS-*g*-PTHF) with controlled backbone length, grafting sites, and spacing length. In this method, first, RAFT polymerization of styrene (St) was performed by using polytrithiocarbonate as chain transfer agent to produce trithiocarbonate-containing polystyrene (PS); the experimental results show that the chain length of the backbone and PS chain between neighboring trithiocarbonate units can be well-controlled. Second, trithiocarbonate-containing PS reacted with maleic anhydride (MAh) to form MAh-containing PS; thus, grafting points were inserted into the PS backbone between St and trithiocarbonate units. Third, poly(ethylene glycol methyl ether) (PEGM) or poly(tetrahydrofuran) (PTHF) chains were linked onto the main chain by esterification reaction of maleic anhydride with PEGM or PTHF to form graft copolymers (PS-*g*-PEGM with $M_n = 24\,900$ and $M_w/M_n = 2.1$; PS-*g*-THF1 with $M_n = 38\,000$ and $M_w/M_n = 1.86$; PS-*g*-PTHF2 with $M_n = 56\,000$ and $M_w/M_n = 1.92$) with controlled backbone length, grafting sites, and spacing length.

Introduction

In recent years, many scientists are interested in creating specialized copolymers of various architectures for new properties.[1] One such set of copolymers is graft copolymers due to that graft copolymers exhibit good phase separation[2] and are used for a variety of applications, such as impact-resistant plastics, thermoplastic elastomers, compatibilizers, polymeric emulsifiers, hydrogels, and gas permeation membranes.[3] Moreover, they generally have low melt viscosity, which is advantageous for processing. Since graft copolymers have many structural variables (composition, backbone length, branch length, branch spacing, etc.), they have great potential to realize new properties. To synthesize graft copolymers with specific properties, the structural variables must be controlled. So far, some structural variables of graft copolymer, such as composition, backbone length, and branch length, can be controlled; however, the branch spacing and positions of the side chains are very difficult to control even using the living polymerization method.[2] The macromonomer method is one of the most useful ways to prepare well-defined graft copolymers.[4] However, the macromonomer method is still deficient in controlling the spacing length and grafting sites because the reactivity ratios of macromonomer and comonomer influence the spacing length and grafting sites, which were affected by many factors, such as the chemical structures of the macromonomer and the comonomer, the kinetic excluded volume associated with the large size of the macromonomer, and the potential incompatibility of the macromonomer and propagating comonomer chain.[5] We are therefore engaged in a research program aimed at the synthesis of graft copolymer with defined grafting sites and controlled branch spacing length.

Recently, great interest in reversible addition−fragmentation transfer (RAFT) polymerization has been reported due to that it not only can be applied to a wide range of monomers under a broad range of experimental conditions as compared with ATRP, SFRP, and ROP techniques, but also provides an easy method to prepare polymers with complex structure.[6−19] Recently, Endo and our research groups have found that polymer having trithiocarbonate moieties in the main chain can be applied as a polymeric precursor to synthesize a sequence-ordered polymer, whose repeating trithiocarbonate unit in the main chain can be arranged with a desired distance by RAFT polymerization of fresh monomer using this trithiocarbonate-containing polymer as chain transfer agent.[20,21]

This paper reports a novel method for the synthesis of graft copolymers with defined grafting sites, homogeneously spaced branches, and controlled backbone length by using polymer **1** as a polymeric precursor. The synthetic procedure is illustrated in Scheme 1. A sequence ordered polymer **2** with controlled distance between sequentially spaced trithiocarbonate functional group was prepared by RAFT polymerization of styrene. Polymer **2** reacted with excess maleic anhydride, and anhydride units were inserted into the PS backbone between the trithioarbonate unit and St unit, forming polymer **3** with sequentially spaced anhydride and trithiocarbonate functional groups in the backbone. Using these anhydride units as grafting points, PS-*g*-PEGM and PS-*g*-PTHF with well-controlled backbone length, grafting sites and spacing length were successfully produced by esterification reaction of anhydride with monohydroxy PEGM and PTHF, respectively.

Experiment Section

Materials. Styrene (St) (Shanghai Chem. Co.) was washed with an aqueous solution of sodium hydroxide (5 wt %) three

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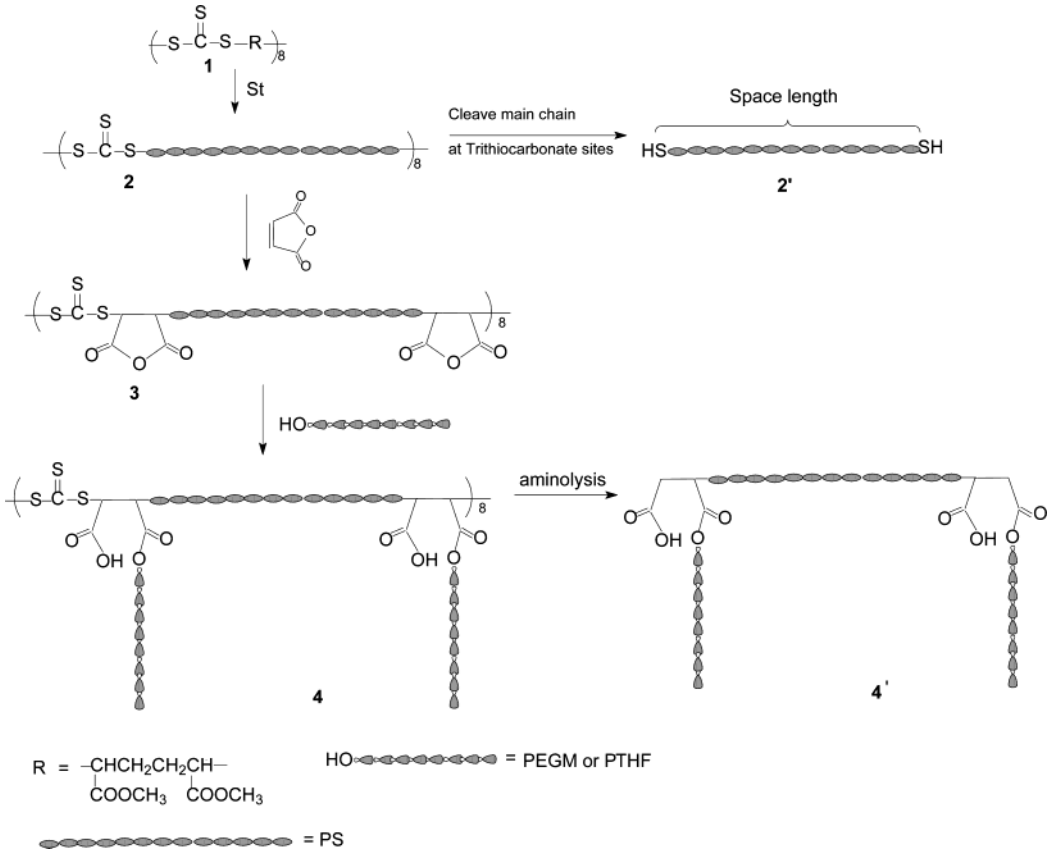
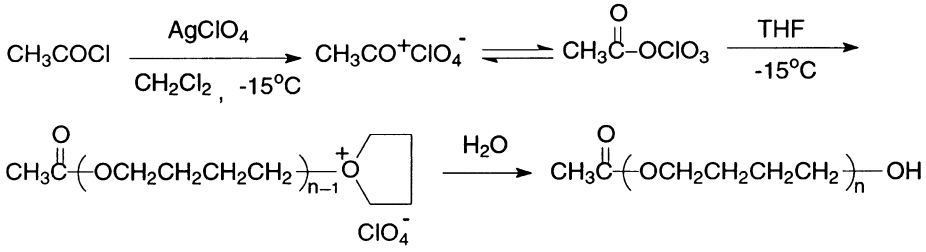
Scheme 1



Scheme 2



times and then washed with water until neutralization. After being dried with anhydrous magnesium sulfate, St was distilled under reduced pressure. Maleic anhydride (MAh) (Shanghai Chem. Co.) was sublimed at 50 °C/2.5 kPa and then stored at −20 °C. THF was distilled from a purple sodium ketyl solution, and dichloromethane was distilled from CaH_2. Silver perchlorate ($AgClO_4$) was prepared in this laboratory and dried at 110 °C for 24 h before use. PEGM-OH (M_n = 550, M_w/M_n = 1.10) was bought from Shanghai Chem. Co. All the other reagents were treated as standard method prior to use.

Synthesis of Polytrithiocarbonate. The synthesis of polymer **1** was based on ref 20.

Synthesis of PTHF-OH. PTHF-OH was synthesized by cationic ring-opening polymerization of THF with acetyl chloride in conjunction with silver perchlorate as initiator as shown in Scheme 2. A typical procedure was as follows. A 150 mL, two-necked flask with a magnetic bar was alternately evacuated and purged with pure nitrogen three times. Into the flask, 30 mL of dichloromethane and 0.47 g (6.0 mmol) of acetyl chloride were added. Then, 1.4 g (6.6 mmol) of silver perchlorate was transferred into the flask at −15 °C under a nitrogen atmosphere. After stirring for 1 h, 60 mL (0.738 mol) of THF was added at −15 °C. Then, the reaction was carried out for a prescribed time, and the sample was withdrawn from the system so that the conversion and molecular weight could be measured. The polymerization was stopped by the addition of excess water to the reaction mixture. The polymerization solution was filtered for the removal of AgCl, and PTHF-OH was purified by the addition of the polymer solution to methanol at −30 °C. The final PTHF-OH was precipitated, collected by filtration, and dried at 40 °C in vacuo. ^{1}H NMR (500 MHz, $CDCl_3$): δ (TMS, ppm) 4.07 ($CH_3COOC\boldsymbol{H}_2$-CH_2), 3.5 (−$C\boldsymbol{H}_2CH_2CH_2C\boldsymbol{H}_2O$−), 2.0 ($C\boldsymbol{H}_3COOCH_2$−), 1.5 (−$OCH_2C\boldsymbol{H}_2C\boldsymbol{H}_2CH_2O$−).

RAFT Polymerization of St Using Polymer 1 as Chain Transfer Agent. A 20 mL glass ample containing AIBN (4.0 mg) was fed with polymer **1** (800.0 mg) and St (16.0 g). It was degassed, sealed off under vacuum, and heated at 110 °C for a prescribed time. After the glass ample was cooled to room temperature, polymer **2** was isolated by precipitation with hexane.

Preparation of MAh-Containing PS. Polymer **2** (M_n = 16 900 g/mol, 8.0 g), MAh (4 g, 40 mmol), and THF (4 mL) were added into a 20 mL glass tube, followed by a freeze−vacuum−thaw cycle three times. The tube was sealed under vacuum and immersed in an oil bath thermostated at 80 °C. After reaction for 24 h, the tube was cooled to room temperature, polymer **3** was precipitated by pouring reaction solution in THF into petroleum ether (bp 30−60 °C) three times, and the excess MAh was removed. The yield was 81%.

Linking PTHF onto the Backbone. Polymer **3** (M_n(GPC) = 19 100 g/mol, 0.5 g), PTHF-OH1 (3.0 g), or PTHF-OH2 (4.0

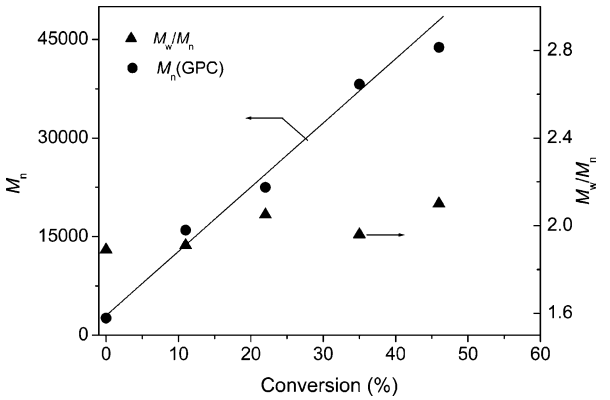


Figure 1. Relationships of M_n(GPC) (●) and M_w/M_n (▲) for polymer **2** with St conversion.

g) and THF (2 mL) were added into a 25 mL one-necked round flask equipped with a magnetic bar. After being flushed with nitrogen for 3 min, the flask was sealed, and the reaction was carried out for 48 h. When the reaction mixture was cooled to room temperature, PS-*g*-PTHF was precipitated by pouring reaction solution in THF into methanol three times at room temperature, and the excess PTHF-OH was removed (PTHF-OH is soluble in methanol at 25 °C and insoluble in methanol at −30 °C).

Linking PEGM onto the Backbone. Polymer **3** (M_n(GPC) = 19 100 g/mol, 5.0 g), PEGM (M_n = 550 g/mol, 5.0 g), and THF (10 mL) were added into a 25 mL one-necked round flask equipped with a magnetic bar. After being flushed with nitrogen for 3 min, the flask was sealed, and the reaction was carried out for 48 h. When the reaction mixture was cooled to room temperature, PS-*g*-PEGM was precipitated by pouring reaction solution in THF into petroleum ether (bp 30−60 °C) three times, and the excess PEGM was removed.

Cleavage of Polymer 2 at Trithiocarbonate Units. Polymer **2** (0.50 g) was dissolved in THF (2 mL) solution of ethylenediamine (1.0 mL), and then this mixture was stirred at 50 °C for 12 h. PS with two thiol ends was obtained by adding the mixture into hexane, collected by filtration, and dried in a vacuum oven at 40 °C. The yield was 68%.

Cleavage of Polymer 4 at Trithiocarbonate Sites. PS-*g*-PTHF (0.5 g) was dissolved in a THF (2 mL) solution of butylamine (2.0 mL), and then this mixture was stirred at 60 °C for 24 h. Cleavage product was obtained by adding the mixture into hexane, collected by filtration, and dried in a vacuum oven at 40 °C. The yield was 59%.

Characterization. ^{1}H NMR spectra were recorded on a Bruker DMX-500 nuclear magnetic resonance instrument, with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. The molecular weight, M_n(GPC), and molecular weight distribution (MWD) were determined on a Waters 515 gel permeation chromatograph (GPC) equipped with three Waters styragel columns, 10^4, 10^3, and 500 Å (column, injection, and refractor meter temperature 35 °C; injection volume, 100 μL); standard narrow polydispersity polystyrene was used in the calibration (calibration range is 500−390 000), THF was used as eluent at a flow rate of 1.0 mL/min, and the refractive index detector was a Waters 410. Infrared spectra were recorded on a Bruker VECTOR-22 IR spectrometer.

Results and Discussion

RAFT Polymerization of St Using Polytrithiocarbonate as Chain Transfer Agent. Polymer **1** containing eight trithiocarbonate units was synthesized according to ref 20. Previous research showed that this polymer can be used as a polymeric precursor to the synthesis of a sequence ordered polymer by insertion polymerization of fresh monomers into the main chain by the RAFT mechanism.[21] The results of the RAFT polymerization of St were illustrated in Figure 1. It is clear that the M_n(GPC) of polymer **2** developed almost linearly with the conversion of St, which indicates that the length of the polymer backbone obtained can be controlled. After 6 h polymerization, the GPC peak of

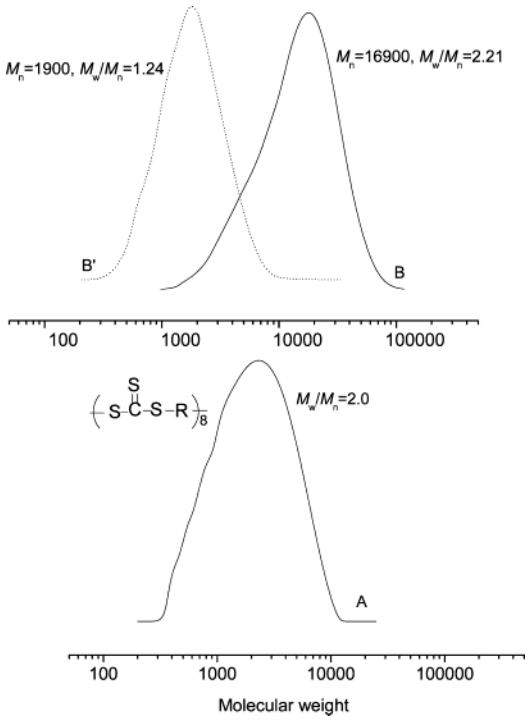


Figure 2. GPC traces of polymer **1** (A), polymer **2** (B) with M_n = 16 900 g/mol, and polymer **2′** (B′) with M_n = 1900 g/mol.

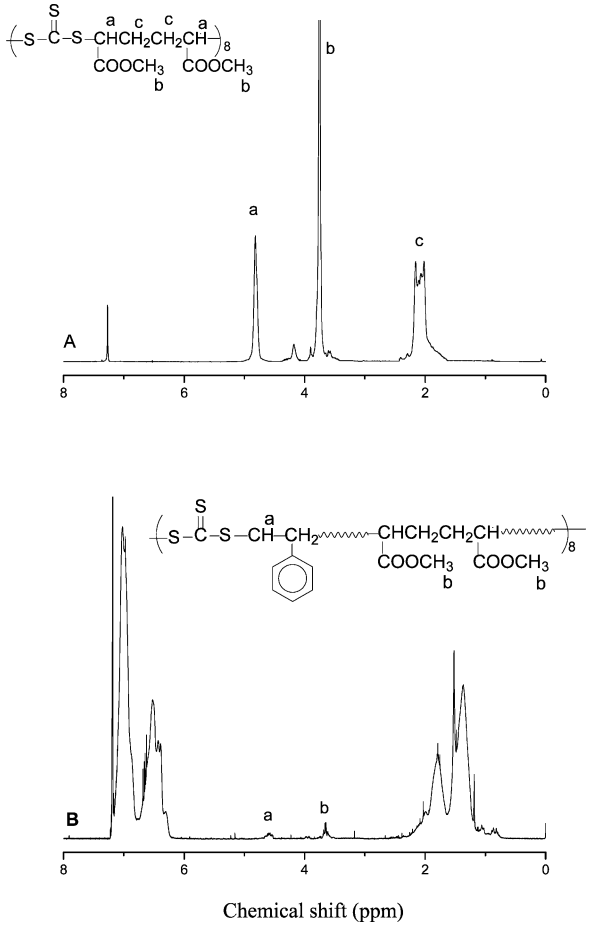


Figure 3. ^{1}H NMR spectra of polymer **1** (A) and polymer **2** (B) with M_n of 16 900.

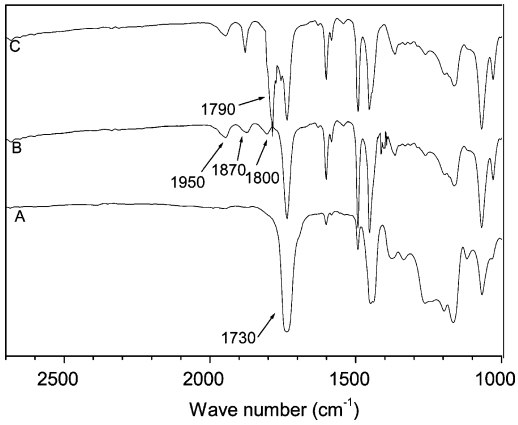


Figure 4. FT-IR spectra of polymer **1** (A), polymer **2** (B) with M_n of 16 900, and polymer **3** (C) with M_n of 19 100.

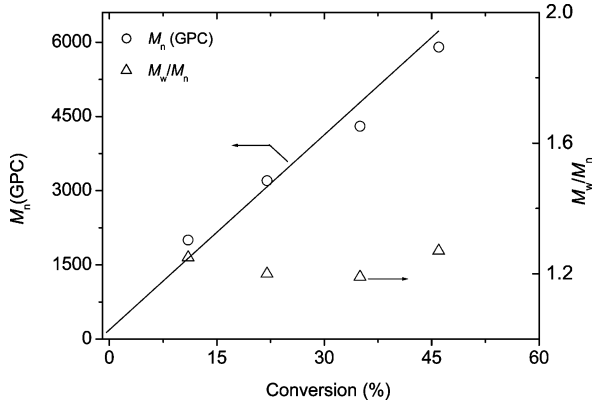


Figure 5. Variations of M_n(GPC) (○) and M_w/M_n (□) for the aminolysis product (**2′**) with St conversion.

the polymer obtained shifted toward the higher molecular weight region as shown in Figure 2, indicating successful preparation of trithiocarbonate-containing PS. A typical ^{1}H NMR spectrum of **2** is shown in Figure 3B. Comparison of ^{1}H NMR spectrum of **2** with that of **1**, the characteristic peaks at $\delta = 6.0-7.2$, 1.2−2.5 ppm for PS and a new small peak at $\delta = 4.65$ ppm appeared while the small peak $\delta = 4.8$ ppm in Figure 3A is absent from Figure 3B, which results from that the C−S bond connecting the trithiocarbonate unit with the methine group in **1** was cleaved, and a new C−S bond connecting the trithiocarbonate unit with the St unit formed. For further verification, FT-IR spectroscopy was performed. The FT-IR spectra of **1** before and after RAFT polymerization of St are shown in Figure 4A,B. Besides the characteristic carbonyl absorption of ester around 1730 cm^{-1} in Figure 4A, new characteristic absorptions of PS in the ranges 1800−2000 and 1450−1650 cm^{-1} were also found. All the facts above proved that trithiocarbonate-containing PS has been successfully prepared by RAFT polymerization.

On the basis of previous research, the space length between two neighboring trithiocarbonate groups should be "equal"; that is, trithiocarbonate groups were embedded in PS backbone homogeneously.[21] A way to confirm this is to chemically cleave PS backbone at trithiocarbonate sites.[21] This can be achieved by aminolysis of **2** in THF solution of ethylenediamine, and PS with two thiol ends was obtained. The molecular weight (M_n-(GPC)) of the cleaved product (2′) is shown in Figure 5, M_n(GPC) for the cleaved product (**2′**) also developed linearly with the conversion of St, and molecular weight distribution (M_w/M_n) was narrow, which indicates that

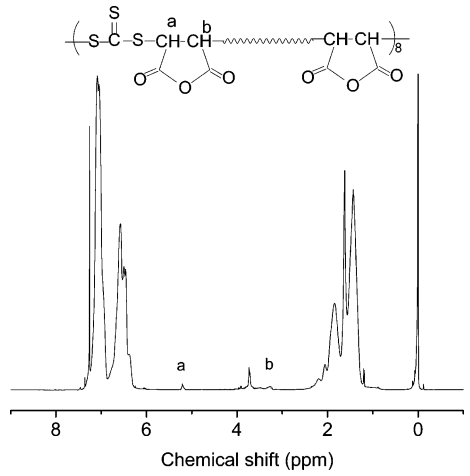


Figure 6. ^{1}H NMR spectrum of polymer **3** with M_n of 19 100.

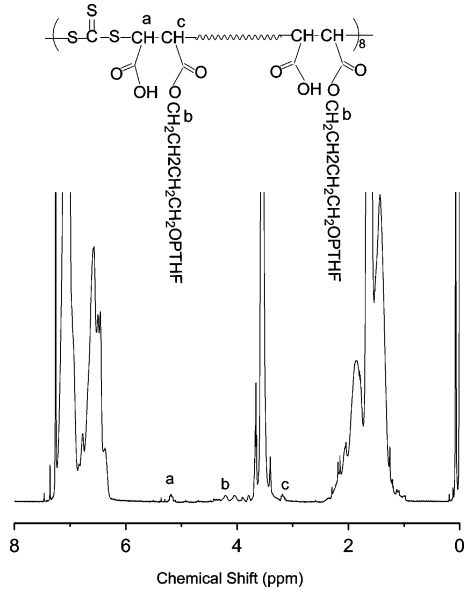


Figure 7. ^{1}H NMR spectrum of PS-*g*-PTHF with M_n of 38 000.

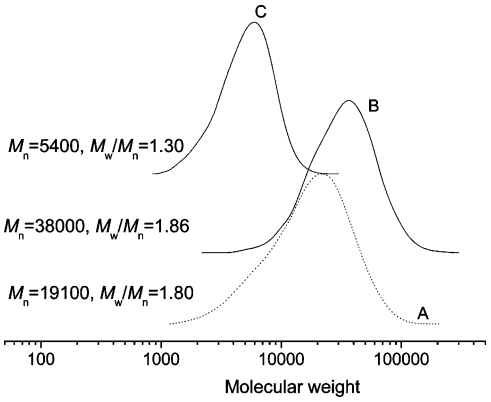


Figure 8. GPC traces of polymer **3** (A), PS-*g*-PTHF (B), and the product (**4′**) of PS-*g*-PTHF cleaved at trithiocarbonate (C).

the space length can be controlled and the spacing distribution of trithiocarbonate units in PS backbone was homogeneous.

Insertion of Grafting Point (MAh) into the PS Backbone. To prepare graft copolymers by the "grafting onto" method, we should insert the grafting point, MAh, into the PS backbone. MAh is a kind of special monomer, and it was reported that only one MAh unit could be inserted into polySt-Br at the bromide site by

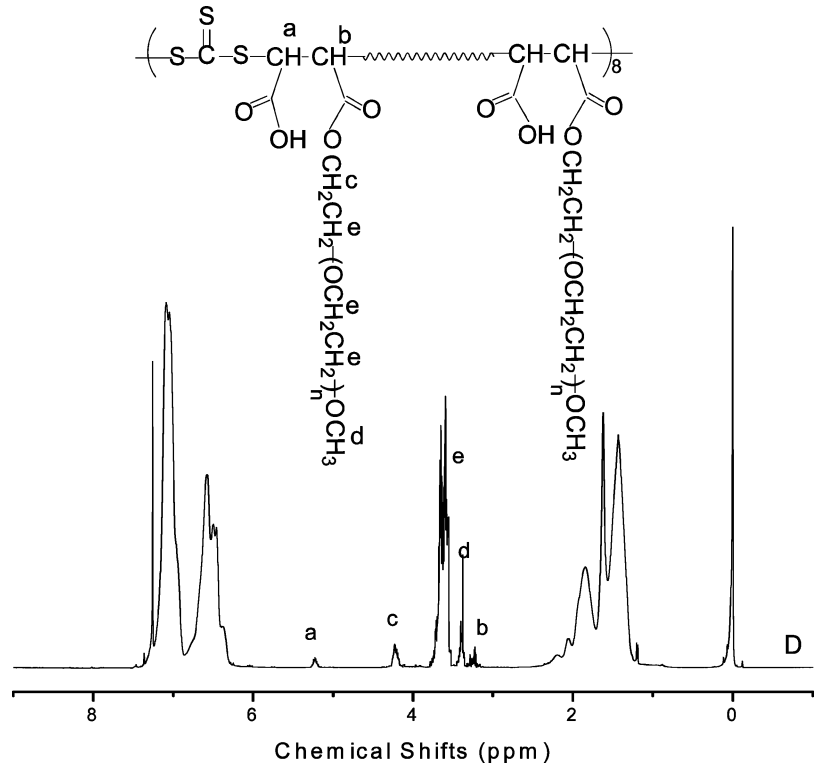


Figure 9. ^{1}H NMR spectrum of PS-*g*-PEGM with M_n of 24 900.

ATRP or polySt-SC(S)Ph chain at the dithiobenzoate site by RAFT to form polySt-MAh-Br or polySt-MAh-SC(S)Ph if polySt-Br or polySt-SC(S)Ph was reacted with excess MAh.[22] In our experiment, we inserted MAh into PS backbone between trithiocarbonate unit and St unit to produce grafting point in PS backbone by the RAFT process of excess MAh with polymer **2**, as shown in Scheme 1. The molecular weight (M_n(GPC)) of **3** increased from 16 900 to 19 100 g/mol after MAh units were inserted into the PS backbone. A typical ^{1}H NMR spectrum of polymer **3** is shown in Figure 6. The peaks at 6.0−7.2 and 1.2−2.5 ppm are the characteristic signals of PS segments. A new peak *a* at 5.2 ppm corresponds to the signal of the methine proton of MAh unit next to trithiocarbonate unit, and the peak *b* at 3.2 ppm corresponds to the other methine proton of MAh unit neighboring St unit. In the meantime, the peak at 4.65 ppm is absent from Figure 6, which resulted from that C−S bond connecting St unit and trithiocarbonate unit was cleaved, and a new C−S bond connecting trithiocarbonate unit with MAh unit formed. The integration ratio of *a*:*b*:*c* is equal to 1:1.1:3.4, indicating that almost no trithiocarbonate group is lost during the MAh inserting reaction and almost each side of trithiocarbonate group is inserted with one MAh unit. For further verification, FT-IR spectroscopy was performed. The FT-IR spectra of **2** before and after insertion MAh are shown in Figure 4B,C. Comparing parts C and B of Figure 4, a new strong absorption around 1790 cm^{-1} is clear in Figure 4C. This is the characteristic carbonyl stretching bands of the anhydride, confirming the existence of anhydride group in PS backbone.

Linking PTHF onto the Backbone. The esterification of **3** with PTHF-OH (M_n(GPC) = 1800 or 3200 g/mol) should afford the graft copolymers with homogeneous spacing distribution. This esterification reaction was carried out according to a procedure similar to the Kallitsis method.[22] The reaction continued for 48 h in order to obtain a good esterification yield. PS-*g*-PTHF was obtained by precipitation in methanol at room temperature, and the results are shown in Table 2. A typical ^{1}H NMR spectrum and the GPC trace of PS-*g*-PTHF were shown respectively in Figure 7 and Figure 8. In Figure 8, it is clear that the GPC curve of PS-*g*-PTHF shifted toward high molecular weight position with respect to the GPC curve of polymer **3**, indicating that the PTHF was successfully grafted onto the PS backbone at anhydride sites. The ^{1}H NMR spectrum shown in Figure 7 also verified this phenomenon. Besides the characteristic peaks of PS at 6.0−7.2 and 1.2−2.5 ppm, the characteristic PTHF peaks at 3.6 and 1.5 ppm also appeared. The appearance of small peak at 4.2 ppm resulted from ester methylene formation of PTHF by esterification reaction of MAh with HO-terminated PTHF. The integral ratio of peaks at 5.2 and 4.2 ppm, which correspond to methine proton of MAh unit next to trithiocarbonate moiety, ester methylene protons of PTHF next to MAh, is equal to 1:1.83, which indicates that more than 90% anhydrides have reacted with PTHF-OH. The cleaved product of PS-*g*-PTHF at trithiocarbonate sites to give PTHF-*b*-PS-*b*-PTHF also

Table 1. Conditions and Results of the Cationic Ring-Opening Polymerization of THF with Acetyl Chloride and $AgClO_4$ as an Initiator System

	time (h)	yield (%)	M_n(GPC)	M_w/M_n
PTHF-OH1	5	18	1800	1.26
PTHF-OH2	7	33	3200	1.20

Table 2. Results of Graft Copolymers

	yield (%)[a]	M_n(GPC) × 10^{-4} [b]	M_w/M_n[b]
PS-*g*-PTHF1	78	3.80	1.86
PS-*g*-PTHF2	69	5.60	1.92
PS-*g*-PEGM	71	2.49	2.10

[a] Yield (%) was based on the ratio of the weight of graft copolymers obtained to theoretical weight. [b] M_n(GPC) and M_w/M_n were measure on GPC.

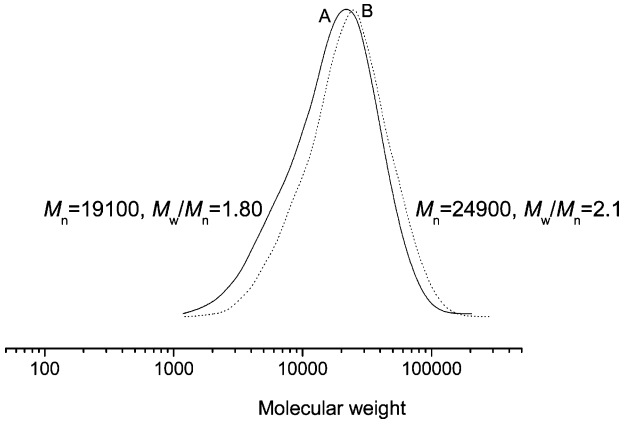


Figure 10. GPC traces of polymer **3** (A) and graft copolymer of PS-*g*-PEGM (B).

has a narrow M_w/M_n (1.30) and much smaller molecular weight than that of PS-*g*-PTHF as shown in Figure 8C. All these facts indicated that PS-*g*-PTHF with well-defined grafting sites and controlled spacing length was obtained.

Linking PEGM onto the Backbone. Preparation of PS-*g*-PEGM is similar to that of PS-*g*-PTHF. After **3** was reacted with PEGM-OH (M_n = 550 g/mol), PS-*g*-PEGM with a molecular weight of 24 900 g/mol was obtained by precipitation in petroleum ether. Its typical ^{1}H NMR spectrum and GPC trace of PS-*g*-PEGM are shown respectively in Figure 9 and Figure 10. In Figure 10, it is clear that the GPC curve of PS-*g*-PEGM shifted to high molecular position, indicating that the PEGM has been grafted onto the PS backbone at anhydride sites. In its ^{1}H NMR spectrum shown in Figure 9, besides the characteristic peaks of PS at 6.0−7.2 and 1.2−2.5 ppm, the peaks at 3.6 and 4.2 ppm corresponding to the ether methylene protons and ester methylene protons of PEGM, respectively, also appeared. The integral ratio of peaks at 5.2, 4.2, and 3.5 ppm, which correspond to methine proton of MAh unit next to trithiocarbonate moiety, ester methylene protons, and ending methyl protons of PEGM, respectively, is equal to 1:1.9:2.8, which indicates that about 95% anhydrides have reacted with PEGM. Thus, PS-*g*-PEGM with well-defined grafting sites and controlled spacing length was obtained.

Summary. A novel method was designed to prepare graft copolymers by reaction of maleic anhydride in the PS backbone with monohydroxy-terminated polymer (such as PTHF-OH and PEGM-OH). The experiment showed that the space length can be well controlled and grafting sites located beside trithiocarbonate units; thus, the grafting sites were defined. This method also can be applied to prepare similar graft copolymers with backnone of PMA, PBA, etc., and graft chains of PEGM, PTHF, etc. The effects of space length and location of grafting sites on property of graft copolymers are being studied.

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