

Synthesis and Characterization of Functionalized Syndiotactic Polystyrene Copolymers

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ABSTRACT: Functionalized syndiotactic polystyrene copolymers were synthesized and characterized. The syndiotactic polystyrene copolymers, poly(styrene-co-4-methylstyrene) (sPSMS), were prepared by styrene with 4-methylstyrene with a metallocene/methylaluminoxane catalyst. In addition, grafted copolymers, chemically grafted with isoprene onto an sPSMS backbone [poly(styrene-co-4-methylstyrene)-g-polyisoprene (sPSMS-g-PIP)] were synthesized by anionic grafting polymerization with a metallation reagent. In this study, we also examined the effect of the degree of functionalization (epoxidation) on the polymer

structure of the sPSMS-g-PIP copolymers. Experimental results indicate that the crystallinity of the sPSMS-g-PIP copolymer was lower than that of the ungrafted sPSMS copolymer. Moreover, the epoxy-containing sPSMS-g-PIP copolymer effectively increased the thermal stability more than did the sPSMS-g-PIP copolymer alone. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1038–1045, 2002

Key words: syndiotactic; functionalization of polymers; graft copolymers; metallocene catalysts

INTRODUCTION

Syndiotactic polystyrene (sPS) is characterized by excellent physical properties such as a low dielectric constant, excellent hydrolytic and dimensional stability, good heat stability, chemical resistance, and a low specific density. sPS is extensively used in the electrical/electronic and automotive industries to replace expensive engineering plastics.

However, sPS is limited by inferior adhesion properties, compatibility, and impact resistance, thus limiting its applications as a construction material. The functionalized polymers can serve as interfacial modifiers to improve their adhesion to and compatibility with other materials as well as impact resistance.^{1,2}

In general, the two routes to the functionalization of polymers are direct copolymerization with functional monomers and postmodifications of preformed polymers. Unfortunately, the metallocene catalysts used to prepare sPS and the Ziegler–Natta catalyst normally cannot incorporate functional-group-containing monomers because of catalyst poisoning.³

Direct functionalization is difficult because of the chemical stability of sPS. Recently, Xu and Chung showed the desirability of introducing polar groups onto sPS to improve adhesion and compatibility.⁴ Sulfonation of sPS was described by Order et al.⁵ Hydroxylated sPS was prepared via a poly(styrene-co-4-tert-butylsilyloxy) precursor by Kim et al.⁶ In general, when 4-methylstyrene is introduced to a sPS backbone, the crystallinity of sPS decreases with increases in the 4-methylstyrene content. However, at low 4-methylstyrene content, the sPS copolymer can be functionalized in benzyl groups without destruction of its crystallinity. Among the many possibilities of the chemical modification of sPS, epoxidation is an efficient means of introducing a new reactive group into the polymer backbone. The preparation and characterization of many types of epoxidation of unsaturated polymers are well-studied reactions and have been reported on in recent years.⁷ The epoxidation of polyolefinic compounds with organic peroxyacids has been extensively studied also because oxiranes were prepared by the reaction of ethylenic compounds with peroxybenzoic acid. Our laboratory has synthesized and characterized an amphiphilic graft copolymer consisting of the epoxidation of a sPS backbone grafted with polyisoprene. In this study, we adopted a postpolymerization approach involving the (1) preparation of syndiotactic poly(styrene-co-4-methylstyrene) (sPSMS), resulting from the copolymerization of styrene and

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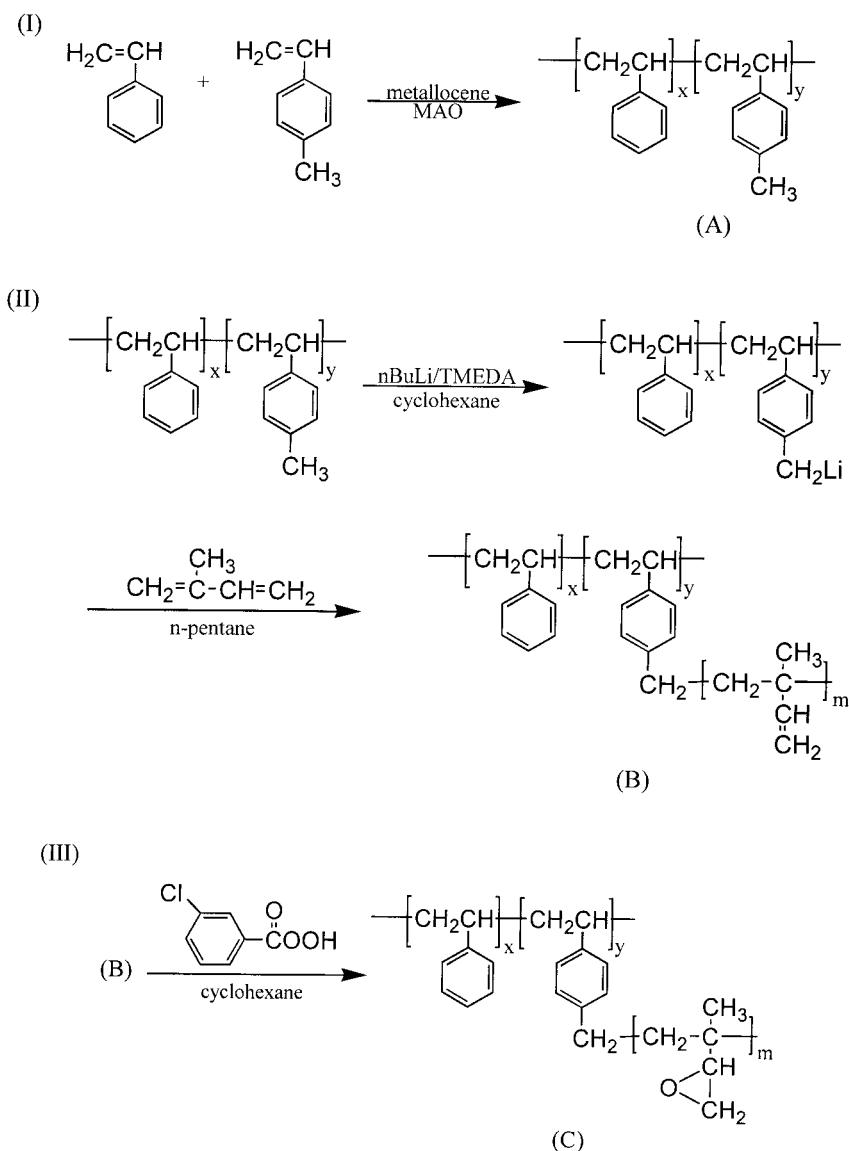


Figure 1 Chemistry used to prepare sPSMS-g-PIPE.

4-methylstyrene; (2) anionic grafting from the reaction of isoprene by a metallation reagent,⁸ and (c) subsequent functionalization by an epoxidation reaction. Additionally, the extent to which the degree of epoxidation affected the polymer structure and the thermal stability of the syndiotactic poly(styrene-co-4-methylstyrene)-g-polyisoprene (sPSMS-g-PIP) copolymers was also investigated.

EXPERIMENTAL

Instrumentation and materials

The temperature range of ¹H-NMR spectra was recorded on a Bruker AM-200 MHz spectrometer (Silberstreifen, Germany). The syndiotactic styrene copolymer was dissolved in either benzene-*d*₆ at an elevated temperature or in chloroform-*d*₁ at room temperature.

The chemical shifts are reported in parts per million relative to tetramethylsilane (TMS). The epoxidation of the polyisoprene moiety in sPSMS-g-PIP was calculated from the corresponding ¹H-NMR spectra. The molecular weights and molecular-weight distributions of the polymers were determined with a Waters 150CV (Milford, MA), which was equipped with three μ Styragel HT columns (Milford, MA) and operated at 140°C. A flow rate of 1 mL/min was used, and the mobile phase was 1,2,4-trichlorobenzene. Number-average molecular weight and weight-average molecular weight (M_w) were calculated on the basis of a narrow molecular-weight distribution polystyrene standard. The thermal properties were measured with thermogravimetric analysis (TGA; PerkinElmer TGA-7; Shelton, CT) and differential scanning calorimetry (DSC; PerkinElmer DSC-7). Thermal decom-

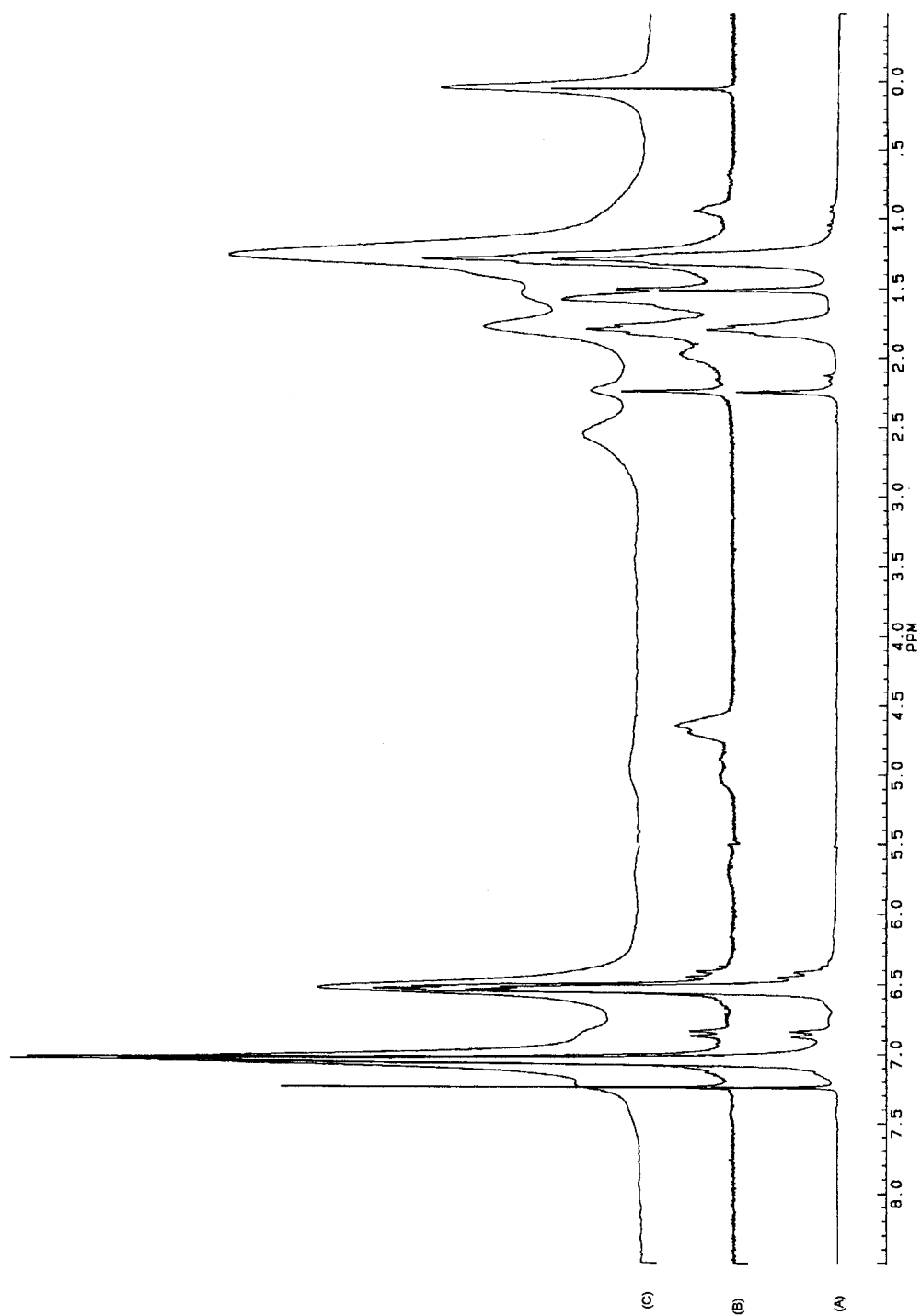


Figure 2 ¹H-NMR spectra of (A) sPSMS copolymer, (B) sPSMS-g-PIP copolymer, and (C) sPSMS-g-PIPE copolymer.

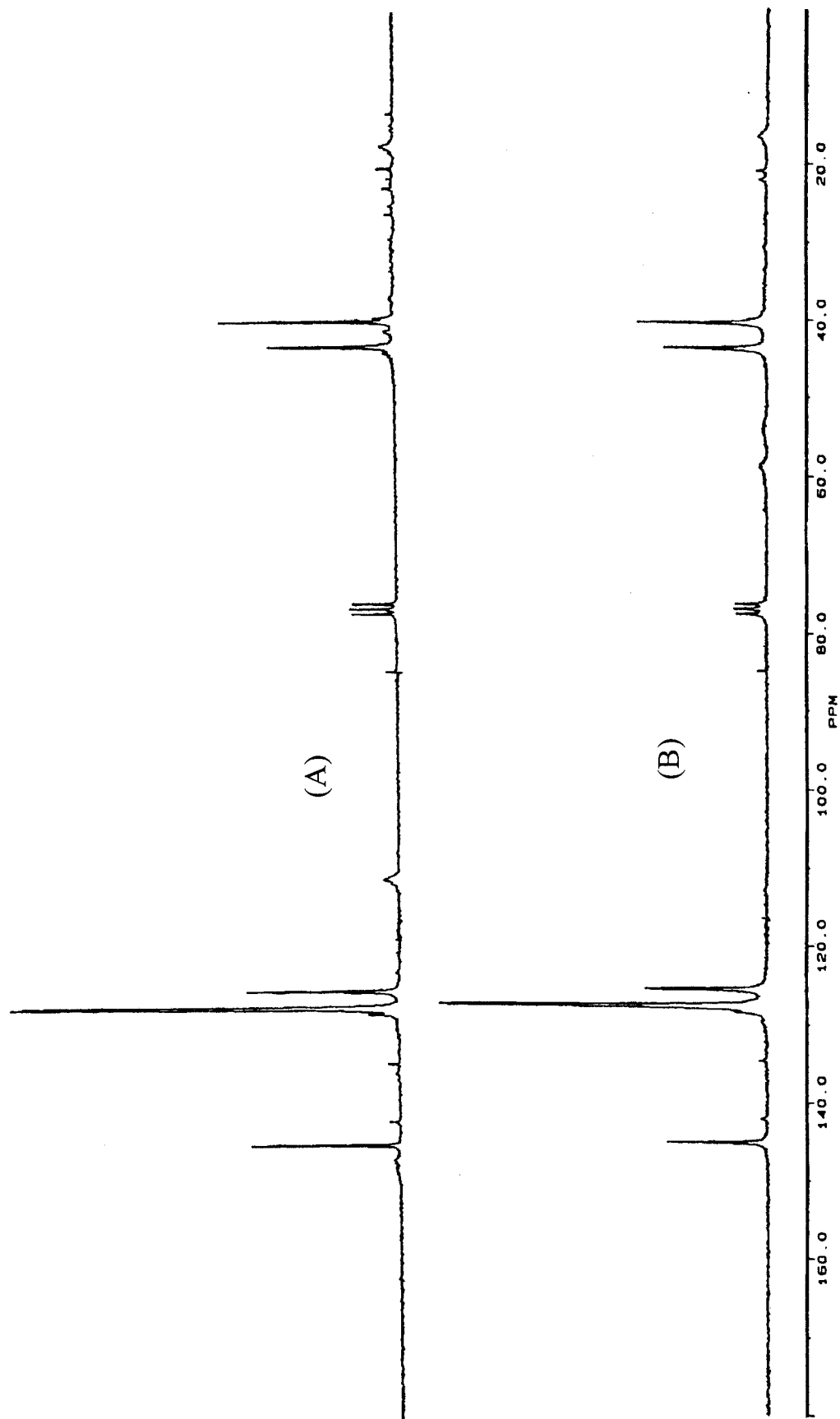


Figure 3 ¹³C-NMR spectra of (A) sPSMS-g-PIP copolymer and (B) sPSMS-g-PIPE copolymer.

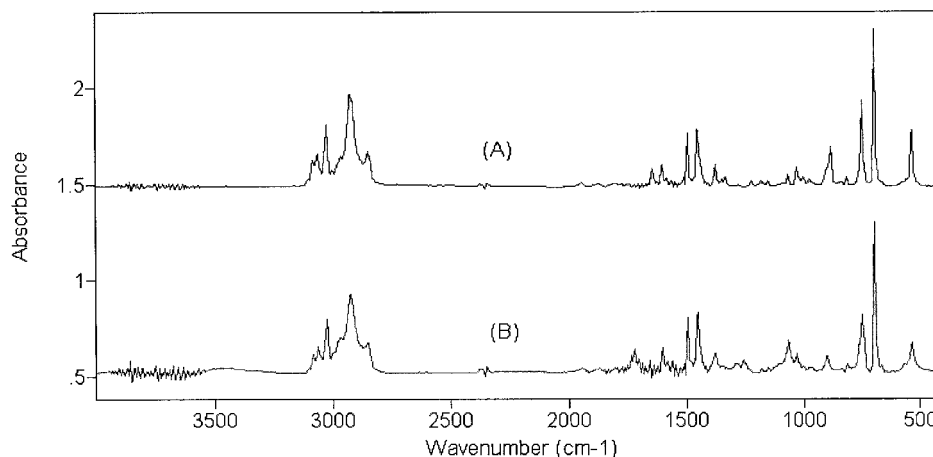


Figure 4 FTIR spectra of (A) sPSMS-g-PIP copolymer and (B) sPSMS-g-PIPE copolymer.

position was studied under a nitrogen atmosphere at a heating rate of 20°C/min. DSC was performed from 30 to 280°C with a typical heating rate of 20°C/min. Fourier transform infrared (FTIR) spectra were recorded at room temperature on a Bio-Rad FTS-135 (Tokyo, Japan) at a resolution of 4 cm⁻¹. We prepared the samples by casting dilute polymer solutions in tetrahydrofuran (THF) onto a KBr plate.

We deoxygenated high-performance liquid chromatography (HPLC)-grade styrene and 4-methylstyrene by N₂ sparge before further purifying them by passing them through a Al₂O₃ column for drying and eliminating the inhibitor. Analytical grade isoprene was dried over calcium hydride for 24 h and then degassed and distilled over a vacuum line into a flask before use.

Synthesis of sPSMS

The copolymerization was carried out in a 5-L steel autoclave (Parr, Moline, IL) with a stirrer at constant pressure (H₂/N₂). Styrene (1800 mL) and 4-methylsty-

rene (180 mL) were added into the reactor via canula. Triisobutylaluminum (4.8 mmol) and methylaluminoxane (MAO; 13.4 mmol) were then charged into the reaction vessel. The reaction vessel was heated to 70°C before 6.75 × 10⁻⁵ mol of pentamethyl-cyclopentadienyl tributylaluminum titanium(III) [Cp*Ti(OBu)₃]⁹ was added. We conducted the reaction for 50 min and terminated it by adding a sodium hydroxide/methanol solution after cooling. The resulting copolymer was purified by Soxhlet extraction with methyl ether ketone for 24 h. The product was filtered and then dried in a vacuum oven at 110°C at least overnight. The resulting copolymer contained about 2.8 mol % 4-methylstyrene with a melting point of 244°C. The gel permeation chromatography (GPC) results indicated a M_w of 54,000. The reaction is shown in Figure 1(I).

Synthesis of sPSMS-g-PIP

In a nitrogen-filled dry box, the sPSMS copolymer was suspended in cyclohexane in a 250-mL round flask

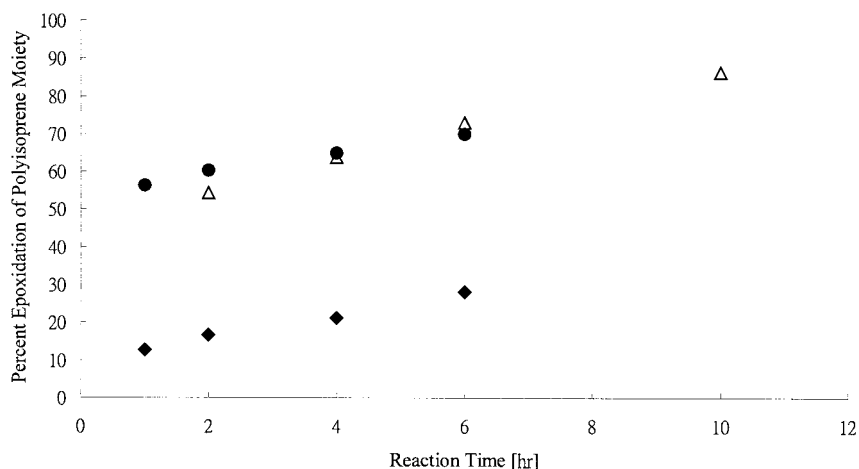


Figure 5 Effect of reaction time and solvent on the degree of epoxidation. The molar ratio of mCPBA to polyisoprene moiety in sPSMS-g-PIP was 2:1. Epoxidation was done with mCPBA in (Δ) CHCl₃, (●) cyclohexane, and (◆) THF.

TABLE I
Effect of the Molar Ratio of mCPBA to the Polyisoprene Moiety on the Degree of Epoxidation in the Cyclohexane Solvent System

Molar ratio of mCPBA to polyisoprene moiety	Degree of epoxidation (%)
0.01	9
0.25	11
0.5	20

with a magnetic stir bar. The flask was then brought out of the dry box and an excess amount of *n*-butyl lithium (*n*-BuLi)/tertramethylethylenediamine (TMEDA; 4-methylstyrene/*n*-BuLi/TMEDA = 1/10/10) solution was added to the flask; the flask was then heated up to 50°C for 15 h under nitrogen. We easily removed the unreacted reagents by filtration and washing the lithiated sPSMS powders with pentane a few times.

Most of the lithiated sPSMS powder was suspended in cyclohexane before isoprene was added. The anionic polymerization took place at room temperature; the reaction continued for 1 hr before it was terminated by the addition of methanol. The resulted grafted copolymer was purified by Soxhlet extraction with pentane for 24 h to remove any homopolyisoprene. The reaction is shown in Figure 1(II).

Epoxy-containing poly(styrene-co-4-methylstyrene)-*g*-polyisoprene (sPSMS-*g*-PIPE)

A dried 100-mL one-necked flask was charged with a solution of 0.5 g of sPSMS-*g*-PIP (1.96 mmol of double bonds) suspended in cyclohexane, followed by the addition of 0.33 g (1.96 mmol) of *m*-chloroperoxybenzoic acid (mCPBA). The solution was stirred for 2 h at room temperature in the dark. The polymer was then precipitated in 300 mL of methanol. The precipitated polymer was washed several times with methanol, filtered, and dried in vacuum at 50°C overnight. The reaction is shown in Figure 1(III).

RESULTS AND DISCUSSION

Characterization of syndiotactic copolymers

The chemistry to prepare sPSMS-*g*-PIPE involved three steps as shown in Figure 1. The sPSMS [Fig. 1(A)] copolymer was prepared by the copolymerization of styrene and 4-methylstyrene with a metallocene catalyst, such as [Cp*Ti(OBu)₃]/MAO, which produced a random copolymer with 2.8 mol % 4-methylstyrene. The sPSMS copolymer was then metallated by *n*-butyllithium in the presence of TMEDA. The resulting macroinitiators were reacted with isoprene, which yielded additional isoprene to the suspended metallated polymer and started the anionic graft from polymerization to form a graft copolymer

with well-defined side chains [sPSMS-*g*-PIP; Fig. 1(B)]. Finally, the epoxidation of sPSMS-*g*-PIP [to get sPSMS-*g*-PIPE; Fig. 1(C)] used mCPBA for the introduction of small amounts of oxirane groups into the grafted copolymer.

The formation of the previously mentioned polymers was confirmed by ¹H-NMR, ¹³C-NMR, and FTIR. Figure 2 shows the typical ¹H-NMR spectra of the (A) sPSMS copolymer, (B) sPSMS-*g*-PIP copolymer, and (C) sPSMS-*g*-PIPE copolymer. In the Figure 2(B), there are resonances at 4.5–5.8 ppm derived from protons attached to the double bonds of the isoprene moieties in the polymer.¹⁰ Comparison of Figures 2(B) and 2(C) reveals a new peak at 2.5 ppm, which corresponds to the epoxy protons on the isoprene moieties, which appear in Figure 2(C). Moreover, during the reaction, a decreasing intensity of the peak at 4.5–5.8 ppm and a corresponding increase in the intensity of the peak at 2.5 ppm were observed. Thus, the relative intensity at 4.5–5.8 and 2.5 ppm could be used to estimate the degree of epoxidation. For instance, in the ¹H-NMR spectrum of complete sPSMS-*g*-PIPE copolymer and sPSMS-*g*-PIPE, the peaks at 4.5–5.8 ppm disappeared completely, and the intensity of the peak at 2.5 ppm reached its maximum.

Figure 3(A) shows the ¹³C-NMR spectrum of the sPSMS-*g*-PIP, in which peaks at 110–112 ppm are derived from carbons of the double bonds of the isoprene moieties in the polymer.¹¹ During the epoxidation reaction, Figure 3(B) reveals a decrease in the intensity of the peak at 110–112 ppm and a corresponding increase in the intensity of the epoxy ring at 50–60 ppm.

Figure 4 shows typical FTIR spectra for sPSMS-*g*-PIP and sPSMS-*g*-PIPE copolymers. According to this figure, they obviously differed. The FTIR spectrum of the sPSMS-*g*-PIPE copolymer was characterized by specific epoxide bands at 910 and 1710cm⁻¹. Meanwhile, the absorption intensity at 886 and 1643cm⁻¹ was reported as the band of the double bond of the sPSMS-*g*-PIP. Therefore, during epoxidation, the double bonds of polyisoprene could be transformed into epoxy functional groups, successfully introducing polar groups into the sPSMS-*g*-PIP copolymer backbone. In addition, the epoxidation of the polyisoprene moiety in the sPSMS-*g*-PIP copolymer backbone was cal-

TABLE II
Effect of the Molar Ratio of mCPBA to the Polyisoprene Moiety on the Degree of Epoxidation in the Chloroform Solvent System

Molar ratio of mCPBA to polyisoprene moiety	Degree of epoxidation (%)
1	41
2	72
4	90

TABLE III
Heat of Crystal Fusion for the SPS Copolymers

Copolymer	Heat of crystal fusion (J/g)
sPSMS	30.1
sPSMS-g-PIP	14.6
sPSMS-g-PIPE	18.0

culated from the corresponding $^1\text{H-NMR}$ spectra. The chemical shift at 2.5 ppm could be attributed to the proton attached to the epoxy ring. This observation corresponded to the results reported by Gemmer and Golub¹² and Jian and Hay.¹³ The $^1\text{H-NMR}$ spectra revealed no significant side reactions, such as ring-opening reactions, in this system. The degree of epoxidation (X) of polyisoprene was calculated from the following equation:

$$X = I_e / (I_e + I_d) \times 100\%$$

where I_e is the intensity of the peak at 2.5 ppm and I_d is the intensity of the peak at 4.5–5.8 ppm.

Effect of reaction time and solvent on the degree of epoxidation

For the epoxidation of the sPSMS-g-PIP copolymer, a molar ratio of mCPBA in two times excess to the double bonds in the polyisoprene moiety was used. The effect of reaction time and solvent on the degree of epoxidation is shown in Figure 5. This figure indicates

that the degree of epoxidation of the sPSMS-g-PIP copolymer increased with increasing reaction time for all the solvent systems. In addition, the degree of epoxidation in the THF system was lower than that of the hydrocarbon and chlorinated hydrocarbon solvent systems. These phenomena might have been due to the mechanism of epoxidation processes via ionic intermediates. Dreyfuss and Kennedy¹⁴ and Kwart and Hoffman¹⁵ observed similar results. Furthermore, the effects of the molar ratio of mCPBA to polyisoprene moiety on the degree of epoxidation in the cyclohexane and chloroform solvent systems are shown in Tables I and II, respectively. According to these tables, the degree of epoxidation of polyisoprene moiety in sPSMS-g-PIP copolymer increases with an increasing molar ratio of mCPBA to polyisoprene moiety for the cyclohexane and chloroform solvent system.

Heat stability

This study further investigated the effect of grafting and epoxidation of the sPSMS copolymer on the heat stability by examination of the thermal behavior of the sPSMS, sPSMS-g-PIP, and sPSMS-g-PIPE copolymers with DSC and TGA. The heat of crystal fusion for these copolymers is shown in Table III. The crystal fusion heat of sPSMS and sPSMS-g-PIP were 30.1 and 14.6 J/g, respectively, implying that the crystallinity decreased when the polyisoprene was grafted onto the sPSMS copolymer backbone. This phenomenon might

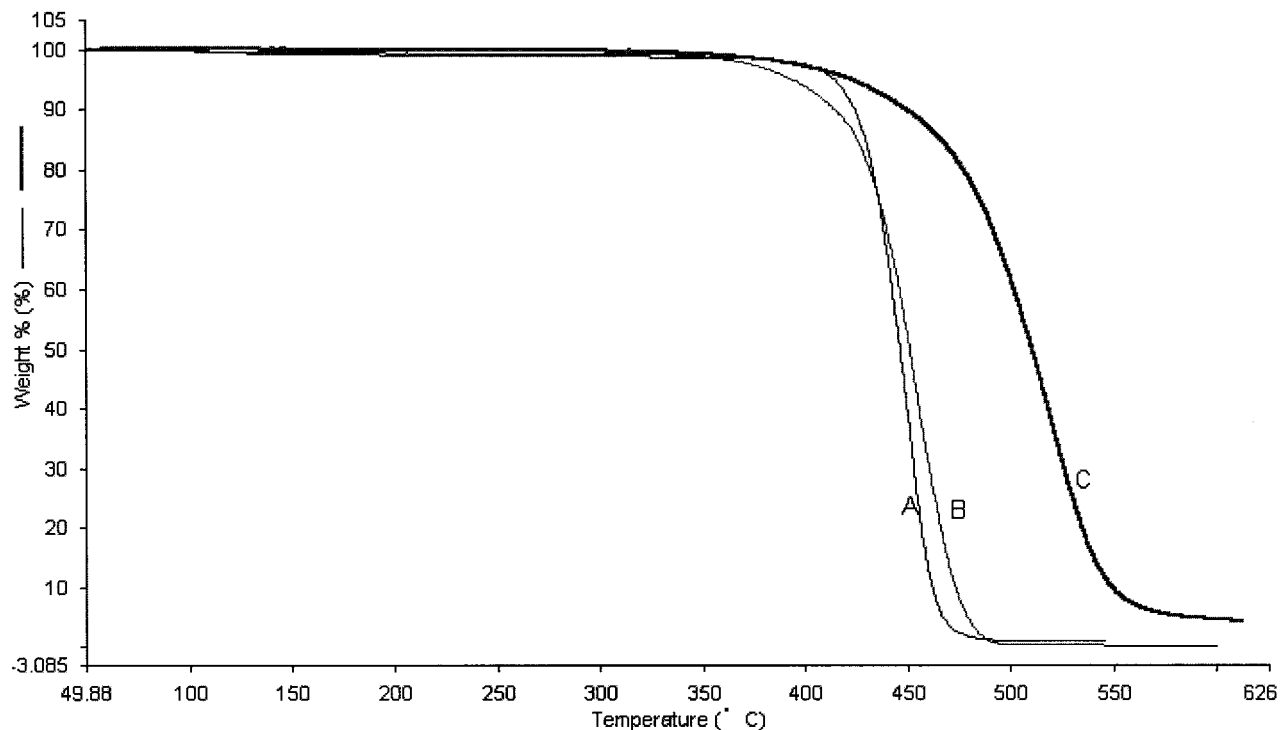


Figure 6 TGA curves of (A) sPSMS copolymer, (B) sPSMS-g-PIP copolymer, and (C) sPSMS-g-PIPE copolymer.

have been due to a bulky pendant group (polyisoprene), which could have resulted in increased steric hindrance. Thus, the packing density of polymer chains decreased, resulting in the decreased crystallinity of the sPSMS-*g*-PIP. However, an opposite phenomenon was observed in the sPSMS-*g*-PIPE copolymer. The heat of crystal fusion of the epoxidation copolymer (sPSMS-*g*-PIPE) was higher than that of the unepoxidated copolymer (sPSMS-*g*-PIP). These results clearly demonstrate that the polymer chain interaction and/or entanglement of the former was higher than that of the latter. This phenomenon might have been due to the epoxy ring of the sPSMS-*g*-PIPE copolymer. Thus, the packing density of the sPSMS-*g*-PIPE copolymer increased, resulting in an increasing heat of crystal fusion. TGA was conducted on the sPSMS, sPSMS-*g*-PIP, and sPSMS-*g*-PIPE copolymers, as shown in Figure 6. According to this figure, the decomposition temperature, at which 10% loss of mass was observed, for these copolymers was higher than 430°C. Thus, a series of sPS copolymers with high thermal stability were obtained. In particular, the sPSMS-*g*-PIPE copolymer showed the highest temperature of 10% loss of mass.

CONCLUSIONS

Well-defined sPS graft copolymers fitted with epoxy groups at grafted chains were prepared in this study. sPSMS-*g*-PIP was prepared by the metallocene copolymerization of styrene and 4-methylstyrene followed by anionic living graft from polymerization. We performed the epoxidation of sPSMS-*g*-PIP by mCPBA,

successfully introducing polar groups into the sPSMS-*g*-PIP copolymer backbone. Experimental results indicate that the degree of epoxidation of the sPSMS-*g*-PIP copolymer increased with increasing reaction time for all the solvent systems. The crystallinity decreased when polyisoprene was grafted onto the sPSMS copolymer backbone.

References

1. Liu, N. C.; Baker, W. E. *Adv Polym Technol* 1992, 11, 249; 1990, 10, 231.
2. Xanthos, M. *Polym Eng Sci* 1988, 28, 1392.
3. Boor, J., Jr. *Ziegler-Natta Catalysts and Polymerizations*. Academic: New York, 1979.
4. Xu, G.; Chung, T. C. *Macromolecules* 1999, 32, 8689.
5. Orler, E. B.; Yontz, D. J.; Moore, R. B. *Macromolecules* 1994, 27, 4774.
6. Kim, K. H.; Jo, W. H.; Kwak, S.; Kim, K. U.; Kim, J. *Makromol Rapid Commun* 1999, 20, 175.
7. (a) Jian, X.; Hay, A. S. *J Polym Sci Part C: Polym Lett* 1990, 28, 285; (b) Davies, C. K. L.; Wolfe, S. V.; Gelling, I. R.; Thomas, A. G. *Polymer* 1983, 24, 107; (c) Udipi, K. *J Appl Polym Sci* 1979, 23, 3311.
8. Chung, T. C.; Lu, H. L.; Ding, R. D. *Macromolecules* 1997, 30, 1272.
9. Tsai, J. C.; Wang, S. J.; Chen, Y. C.; Yang, S. T. U.S. Pat. 3,004,967 (1999).
10. White, J. L.; Shaffer, T. D.; Ruff, C. J.; Cross, J. P. *Macromolecules* 1995, 28, 3290.
11. Hou, H. C.; Tsiang, R. C.; Hsieh, H. C. *J Polym Sci Part A: Polym Chem* 1997, 35, 2969.
12. Gemmer, R. V.; Golub, M. A. *J Polym Sci Polym Chem Ed* 1978, 16, 2985.
13. Jian, X.; Hay, A. S. *J Polym Sci Part A: Polym Chem* 1991, 29, 547.
14. Dreyfuss, P.; Kennedy, J. P. *Anal Chem* 1975, 47, 771.
15. Kwart, H.; Hoffman, D. M. *J Org Chem* 1966, 31, 419.