# Synthesis and Characterization of Graft Copolymers of Syndiotactic Polystyrene with Polybutadiene and 4-Methylstyrene

**Nathinee Srinate, Supakanok Thongyai, Piyasan Praserthdam**

*Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand 10330*

**ABSTRACT:** The basic method for synthesizing syndiotactic polystyrene-*g*-polybutadiene graft copolymers was investigated. First, the syndiotactic polystyrene copolymer, poly(styrene-*co*-4-methylstyrene), was prepared by the copolymerization of styrene and 4-methylstyrene monomer with a trichloro(pentamethyl cyclopentadienyl) titanium(IV)/modified methylaluminoxane system as a metallocene catalyst at 50°C. Then, the polymerization proceeded in an argon atmosphere at the ambient pressure, and after purification by extraction, the copolymer structure was confirmed with ^{1}H-NMR. Lastly, the copolymer was grafted with polybutadiene (a ready-made commercialized unsaturated elastomer) by anionic grafting reactions with a metallation reagent. In this step, poly(styrene-*co*-4-methylstyrene) was deprotonated at the methyl group of 4-methylstyrene by butyl lithium and further reacted with polybutadiene to graft polybutadiene onto the deprotonated methyl of the poly(styrene-*co*-4-methylstyrene) backbone. After purification of the graft copolymer by Soxhlet extraction, the grafting reaction copolymer structure was confirmed with ^{1}H-NMR. These graft copolymers showed high melting temperatures (240–250°C) and were different from normal anionic styrene–butadiene copolymers because of the presence of crystalline syndiotactic polystyrene segments. Usually, highly syndiotactic polystyrene has a glass-transition temperature of 100°C and behaves like a glassy polymer (possessing brittle mechanical properties) at room temperature. Thus, the graft copolymer can be used as a compatibilizer in syndiotactic polystyrene blends to modify the mechanical properties to compensate for the glassy properties of pure syndiotactic polystyrene at room temperature. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 112: 335–344, 2009

**Key words:** graft copolymers; metallocene catalysts; polybutadiene; polystyrene; synthesis

## INTRODUCTION

Syndiotactic polystyrene (sPS) is an important engineering plastic and has excellent physical properties such as a low dielectric constant, high chemical resistance, high hydrolytic resistance, high heat resistance, and good dimensional stability.[1,2] However, although sPS has great physical properties, it has limited applications at low temperatures (lower than room temperature) because of its low compatibility and low impact resistance. Its glass-transition temperature ($T_g$) is higher than room temperature, being approximately 100°C.

Many attempts have been made to characterize new materials and improve the physical and mechanical properties and processability of sPS. The addition of an olefin monomer, especially ethylene, during styrene polymerization to achieve styrene/olefin copolymers has been one of the attempts. The styrene/olefin copolymers have various microstructures, such as random, block, and alternating copolymers, because of the synthesis conditions with a metallocene catalyst.[3] Physical polymer blends are the other choices for accessing feasible sPS modification.[4] In addition, the synthesis of copolymers of sPS with macromonomers or micromonomers is of great interest.

There are many reports about the copolymerization techniques of sPS. For example, Xu and Chung[5] introduced polar groups into sPS to improve adhesion and compatibility. Hydrogenation of a poly(syndiotactic polystyrene-*g*-butadiene) graftlike copolymer was studied by Liu.[3] To effectively increase the thermal stability, an epoxy-containing sPS graft copolymer was prepared with 4-methylstyrene (MS) and a metallocene/methylaluminoxane catalyst by Li et al. Recently, achievements in the stereospecific copolymerization of styrene and butadiene monomers with transition metals have provided alternative ways of improving the mechanical

properties of these materials through the control of the cis selectivity of butadiene segments.[6–9]

Previously, sPS graft copolymers were prepared through the introduction of graft side chains by polymerization with low-molar-mass monomers. In this manner, metallocene polymerization of styrene to obtain sPS and later grafting with the monomer isoprene or the atactic monomer styrene were performed to obtain poly(syndiotactic polystyrene-g-styrene)[4,10] or poly(syndiotactic polystyrene-g-isoprene), respectively.[10,11] The obtained graft copolymers were used as additives via blending with pure sPS. Their polymorphic behaviors were studied with X-ray diffraction, and the results illustrated successful approaches to sPS modification through the use of the aforementioned graft copolymers as compatibilizers. Recently, Ban et al.[12,13] investigated poly(syndiotactic polystyrene-b-cis-butadiene), which was synthesized by the blocking of butadiene monomer to sPS chains for effective compatibilization of an immiscible blend of sPS and cis-polybutadiene (cis-PB). Their block copolymer, poly(syndiotactic polystyrene-b-butadiene), was produced from the reaction with butadiene monomer. However, the sPS–PB copolymer studied in this research was prepared from commercial high-molar-mass PB and was directly grafted to main-chain sPS to obtain poly[poly(styrene-co-4-methylstyrene)-g-polybutadiene] [poly(sPSMS-g-PB)].

In this study, the method of synthesizing a graft copolymer of sPS and PB (a commercial elastomer) via an n-butyl lithium (n-BuLi) reaction was investigated. Many researchers have reported the copolymerization of sPS with low-molar-mass butadiene[12–14] or isoprene monomers,[4,10,11,15] whereas in this article, we report the grafting reactions of sPS and high-molar-mass PB (Scheme 1). The combination of metallocene copolymerization and grafting reaction procedures for the preparation of the graft copolymers is illustrated. As before, the resulting graft copolymers can be used as compatibilizers of an immiscible blend of sPS and high cis-PB. However, in this research, the synthesized graft copolymers were used as additives to pure sPS, and the mechanical properties of the blends were studied with dynamic mechanical analysis.

## EXPERIMENTAL

### Materials

Trichloro(pentamethyl cyclopentadienyl) titanium (IV) (Cp*TiCl$_3$), purchased from Aldrich (USA), and modified methylaluminoxane (MMAO; 1.83$M$ in toluene), donated from Tosho Finechem Co., were used without further treatment. PB, donated by BST Elastomers Co., Ltd. [Thailand; weight-average molecu-
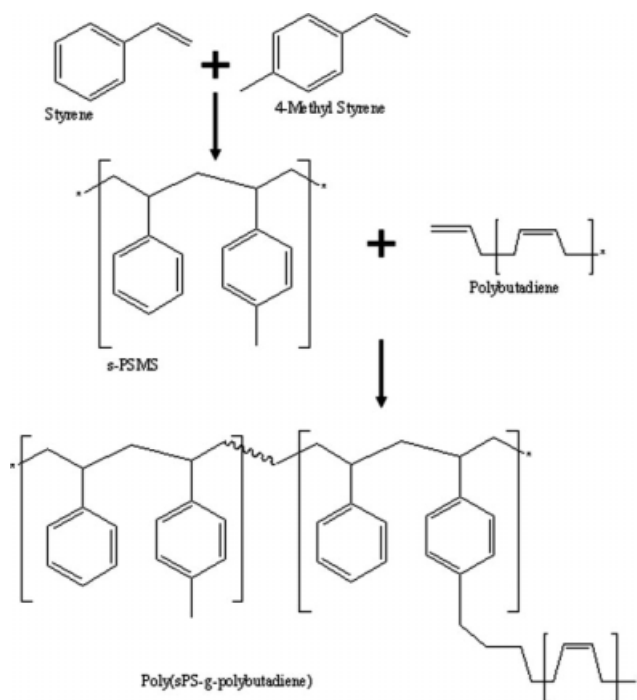
**Scheme 1** Profile of the reactions.

lar weight ($M_w$) = 70 × 10$^4$, number-average molecular weight = 18 × 10$^4$, high cis content = 95% minimum, and ash content = 0.5% maximum], was used without purification. Styrene and MS monomer (Aldrich) were distilled under reduced pressure before use. n-BuLi (Aldrich), potassium tert-butoxide (Fluka), and cyclohexane (Fluka, Switzerland) were also used without purification. Toluene was refluxed over sodium metal and distilled before use. o-Xylene (Aldrich), methyl ethyl ketone (Aldrich), pentane (Aldrich), hydrochloric acid (Aldrich), and methanol (Aldrich) were again used without purification, and polystyrene (PS) standards with molecular weights of 10,000 and 100,000 (Fluka) were used to determine the $M_w$ values of the synthesized copolymers.

### Synthesis of syndiotactic poly(styrene-co-4-methylstyrene) (sPSMS; PS-0)

The syndiotactic copolymerization of PS and MS was carried out. Styrene (78.3 mmol), MS monomer (8.7 mmol), MMAO (30 mmol), and Cp*TiCl$_3$ (0.15 mmol) were injected into a 250-mL glass reactor with magnetic stirring with toluene as a solvent. The reaction was conducted at 50°C under an argon atmosphere for 1 h and terminated by the addition of excess acidic methanol and precipitation of the sPSMS product. The precipitated sPSMS product was washed with acidic methanol to separate the remaining solution, and this was followed by drying *in vacuo* at 60°C. The precipitated product was
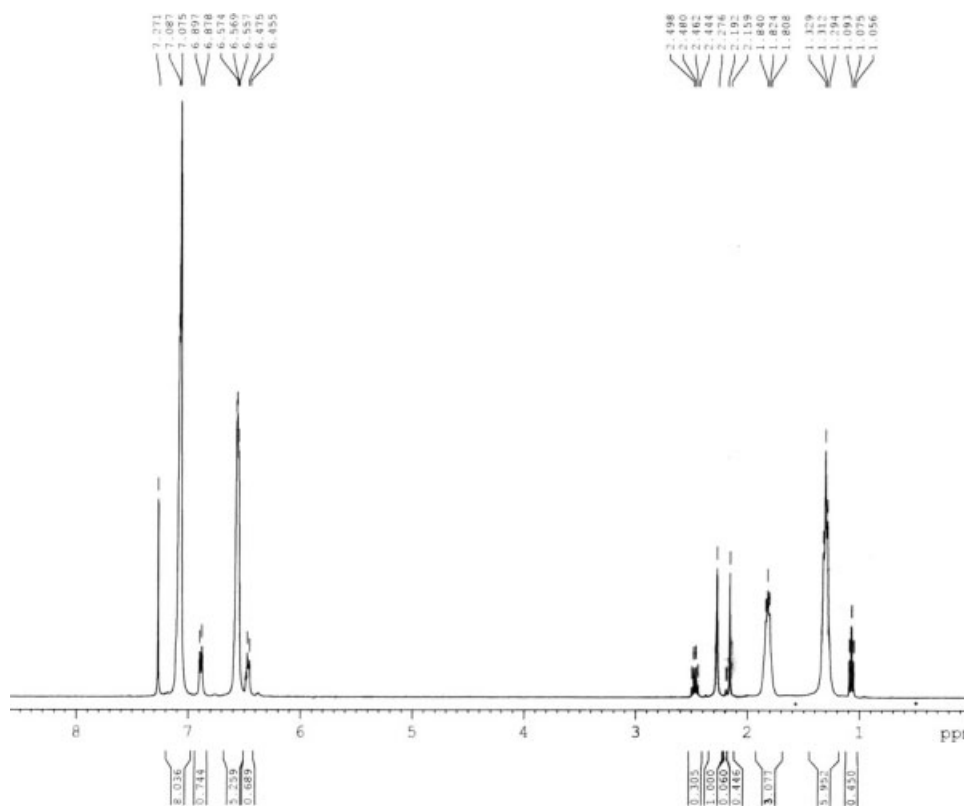
**Figure 1** ^{1}H-NMR spectrum of PS-0 (sPSMS).

purified by Soxhlet extraction with methyl ethyl ketone for 24 h to separate the insoluble sPSMS from other tacticity that might occur. The remaining insoluble copolymer was solely sPSMS, and the other tactic polymers (atactic and isotactic) were dissolved by methyl ethyl ketone and washed away.

**Synthesis of poly(sPSMS-*g*-PB)**

Under an argon atmosphere, the previously obtained sPSMS copolymer (1 g) was suspended with 20 mL of cyclohexane in a 250-mL, round glass reactor with magnetic stirring. Then, 2 mmol of *n*-BuLi and 10 mmol of potassium *tert*-butoxide were added to the reactor. The reaction was conducted at room temperature for 3 h to provide the deprotonated sPSMS powder. The deprotonated polymer was then isolated after filtration by being washed several times with cyclohexane and was dried *in vacuo*.

The deprotonated sPSMS powder (0.5 g) was suspended in 20 mL of cyclohexane before 1 g of PB was added. The grafting reaction took place at room temperature for specific reaction times (0.5, 1, and 2 h for PS-1, PS-2, and PS-3, respectively). It was terminated by the addition of acidic methanol, and the graft copolymer product precipitated. This was then purified by Soxhlet extraction with pentane for 24 h to remove any excess ungrafted PB from poly(syndiotactic polystyrene-*g*-polybutadiene) [poly(sPS-*g*-PB)]. The insoluble poly(sPSMS-*g*-PB) was successively separated and purified from the soluble PB under extraction by pentane.

**Characterization**

The $M_w$ values of the polymers were determined by solution viscosity with an Ubbelohde tube at 95°C in *o*-xylene in comparison with the known $M_w$ values of PS standards. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on an Avance DPX-400 spectrometer (Switzerland). The sPS copolymers were dissolved in *o*-dichlorobenzene and chloroform-$d_1$ at an elevated temperature. The thermal properties were measured with a PerkinElmer (USA) Diamond differential scanning calorimeter at a heating rate of 20°C/min in the temperature range of −60 to 300°C. The differential scanning calorimetry (DSC) temperature cycle commenced with the first heating, cooling, and second heating. The morphology of all sPS copolymers was investigated with a JSM 5410LV scanning microscope (Japan). The samples for SEM analysis were coated with gold particles by an ion-sputtering device to provide electrical contact for the specimens.

The graft copolymer and commercial sPS were blended by a melt-mixing method at 300°C. The blend sample was melted and molded into a film
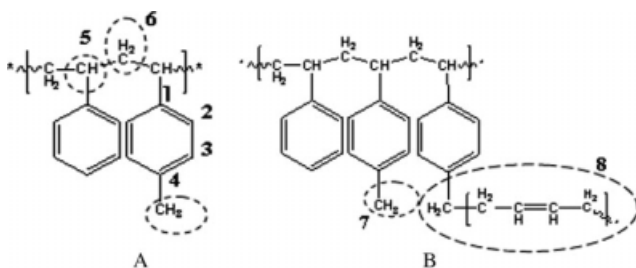
**Figure 2** Structures of the synthesized copolymers: (A) sPSMS and (B) poly(sPSMS-*g*-PB).

sample by a hot-press machine at 280°C. The mechanical properties of the film samples were studied with a PerkinElmer Diamond dynamic mechanical analyzer. The entire experiment was operated at 1 Hz over the temperature range of 40–250°C, and the sample size was $10 \times 50 \times 0.5$ mm$^3$.

## RESULTS AND DISCUSSION

### Synthesis of poly(sPSMS-*g*-PB)

A random copolymer (PS-0), which was synthesized through the copolymerization of styrene and MS with Cp*TiCl$_3$/MMAO as a catalyst, was purified by Soxhlet extraction with methyl ether ketone to separate the insoluble sPSMS from other soluble products (usually other tactic products, e.g., atactic and

isotactic products). The obtained PS-0 (sPSMS) had approximately 32.5 mol % MS, as calculated from the integration of the $^1$H-NMR spectra of sPSMS (Fig. 1) by the ratio of the peak integration at 2.28 ppm representing the methyl proton (—CH$_3$; 1.000) to the peak integration at 1.82 ppm representing the proton in the chain (—CH; 3.077). The proton number of —CH in PS-0 appeared at every benzene ring, regardless of the type of monomer, whereas the proton number of methyl (—CH$_3$) in PS-0 appeared only according to MS. The structure of sPSMS is shown in Figure 2.

The sPSMS copolymer was further metallated by *n*-BuLi under strongly base conditions. PB was added to the metallated sPSMS, and the grafting reactions of PB to sPSMS chains started with the formation of well-defined graft side chains at the methyl group of MS. The PB was a commercialized elastomer with a high cis configuration (>95 wt %). The grafting experiments were conducted with the same amount of sPSMS and PB for each reaction condition. Even if incompletely graft sPSMS existed, PB was added in excess under all conditions. Moreover, the addition of excess amounts of PB led to poly(sPSMS-*g*-PB) in good yields without any difficulty. The synthesis of graft copolymers of sPSMS and PB by the reaction of the CH$_3$ group of MS with *n*-BuLi was successfully conducted and could be proven by $^{13}$C-NMR as follows. The excess PB was removed by Soxhlet extraction with pentane to
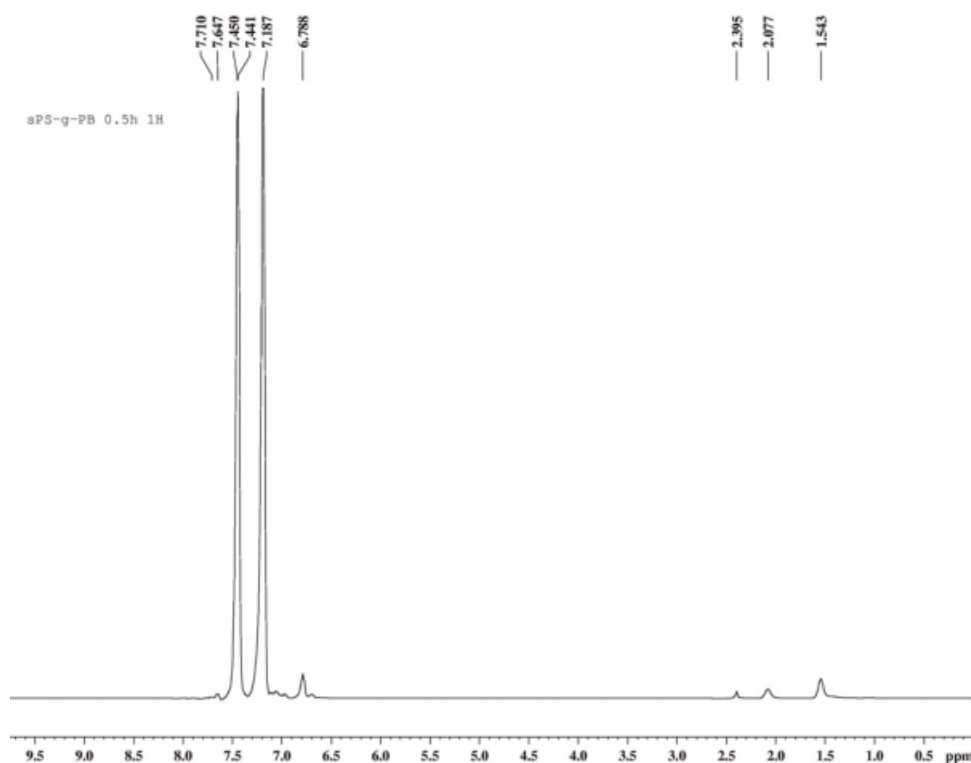


**Figure 3** $^1$H-NMR spectrum of PS-1 (sPS copolymer) in CDCl$_3$/*o*-dichlorobenzene.
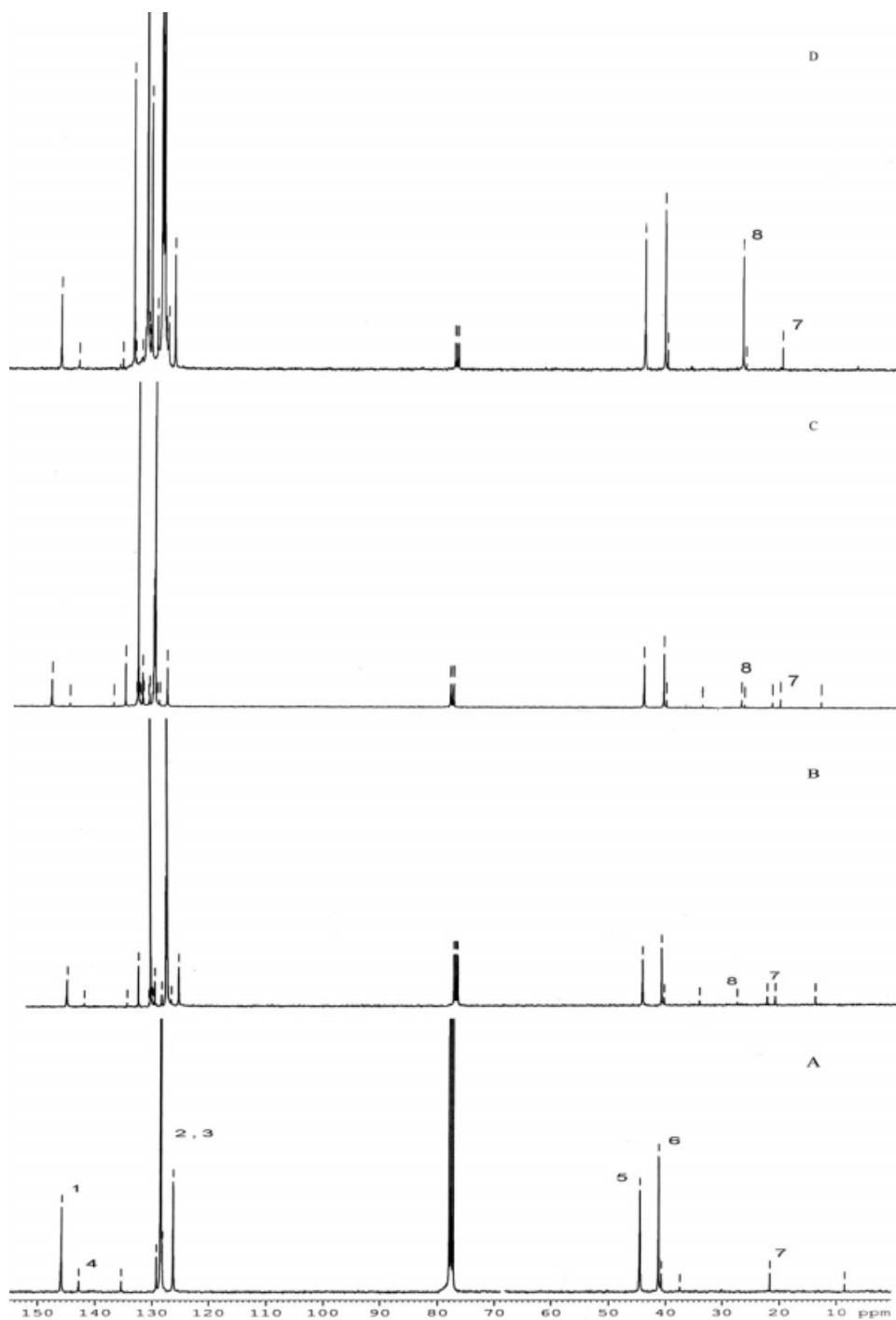
**Figure 4** $^{13}$C-NMR spectra of sPS copolymers in CDCl$_3$/$o$-dichlorobenzene: (A) PS-0 (dissolved in CDCl$_3$ only), (B) PS-1, (C) PS-2, and (D) PS-3.

ensure that excess PB would not interfere with $^{13}$C-NMR.

The graft copolymer structures and positions of each carbon obtained by $^{13}$C-NMR are defined in Figure 2. The main characteristics of the following NMR peaks and the structures in Figure 2 can be correlated. Because of the relatively high molecular weight of these graft copolymers, they could be dissolved only in hot dichlorobenzene. The graft copolymers could not directly dissolve in the solvent CDCl$_3$, so mixed solvents of 5 mL of dichlorobenzene and 1 mL of CDCl$_3$ were used in most systems. The characteristics of the $^{1}$H-NMR spectra only for the graft copolymer of PS-1 are shown in Figure 3. The $^{1}$H spectra showed that the methyl proton (—CH$_3$) was depleted or hardly detected; this was caused by the poor solubility of sample PS-1 and the disappearances of the methyl proton in PS-1 after

**TABLE I**
**Results of the Graft Reaction of sPSMS with PB**

| Sample | sPSMS (g) | PB (g) | Reaction time (h) | Yield (g) | PB (%) | $[\eta]$ (g/dL) | $M_w \times 10^4$ |
|---|---|---|---|---|---|---|---|
| PB[a] | 0.0 | 1.0 | — | — | 100.00 | 0.24 | 35.35 |
| PS-0[b] | 1.0 | 0.0 | — | — | 0.00 | 0.07 | 0.48 |
| PS-1 | 0.5 | 1.0 | 0.5 | 0.85 | 3.94 | 0.11 | 2.17 |
| PS-2 | 0.5 | 1.0 | 1.0 | 1.26 | 11.50 | 0.19 | 17.28 |
| PS-3 | 0.5 | 1.0 | 2.0 | 1.38 | 34.47 | 0.28 | 66.31 |

The grafting reaction conditions were 2 mmol of $n$-BuLi, 0.01 mol of potassium $tert$-butoxide, and 25°C.
[a] $cis$-PB (commercial).
[b] sPSMS (nongraft copolymer).

the reaction from PS-0. Because of the poor solubility of PS-1, the reduction of the methyl peak intensity can represent only the qualitative amount of methyl protons in the graft copolymer and can hardly be compared with the PS-0 spectra in Figure 1.

The characteristics of $^{13}$C-NMR spectra for all the copolymers are shown in Figure 4. Because mixed solvents were used, the NMR peaks could include the dichlorobenzene peaks. The observed peaks can be judged for qualitative purposes only.

The strong and sharp peak appearing at 145.9 ppm confirmed that the graft copolymers were highly syndiotactic.[12,13] Figure 4(A) shows the peaks at 21.4 ppm derived from methyl carbon in MS. Figure 4(B–D) reveals during the anionic grafting reaction a qualitative decrease in the peak intensity at 21.4 ppm and a corresponding qualitative increase in the peak intensity of the PB units at 27.5 ppm. This peak proved that PB was highly cis-1,4.[12,13] If the grafting reaction had been complete, the $^{13}$C-NMR peak at 21.4 ppm should have disappeared completely, and the intensity of the peak at 27.5 ppm should have reached its maximum. However, the peak at 21.4 ppm remained, showing the incomplete depletion of $CH_3$ under all reaction conditions. The PB peak at 133 ppm interfered with the peak of dichlorobenzene, so only the peak at 27.5 ppm PB was verified. The content of PB was calculated from the integration of the $^{13}$C-NMR spectra of the sPS copolymer [Fig. 4(A–C)] by the ratio of the peak integration at 27.5 ppm representing C=C in PB to the peak integration at 45 ppm representing the carbon in the chain as ─CH (1.000).

The conditions and properties of the synthesized grafting copolymers with various reaction times are shown in Table I.

The intrinsic viscosity ($[\eta]$) was calculated from the specific viscosities[16] of various concentrations of the polymer in $o$-xylene at 95°C. The equation that relates $[\eta]$ to $M_w$ is given; the constants were calculated from the $[\eta]$ values of standard PS samples with known $M_w$ values of 100,000 and 1,000,000 (PS100,000 and PS1,000,000, respectively). Table II

shows $[\eta]$ and $M_w$ calculated in the equation with the calculated constants:

$$[\eta] = 0.005558(M_w)^{0.294245046} \qquad (1)$$

According to Table I, the grafting activities, based on the polymer yield, increased with the increase in the reaction time. The amount of PB that was involved could be determined from the molecular weights of these copolymer, which were determined from the solution viscosity (with $o$-xylene as the solvent at 90°C). Because of their high molecular weight, the graft copolymers had very poor solubility.

The $[\eta]$ and $M_w$ values of the copolymers are also summarized in Table I. The PB content increased when the reaction time increased. Furthermore, from a comparison of the results between PS-1 and PS-2 and PS-2 and PS-3, it is obvious that $M_w$ more than doubled as the reaction time increased. We suspected that this system might display cumulative behavior because the molecular weight and PB content increased with the increase in the reaction time, whereas metallated anionic sites still remained the same. Because PB is a macromolecule and could cause steric hindrance, when PB was grafted to the main chain of the copolymer at the methyl group site, its bulky structure could block the grafting reaction at the adjacent methyl groups that were left over. The increase in the molecular weight may have arisen from the commutative results and the new grafting reaction on the remaining anionic sites.

**TABLE II**
**$[\eta]$ Values and Calculated $M_w$ Values**

| Sample | $[\eta]$ (g/dL) | $M_w$ |
|---|---|---|
| PS100,000 | 0.1645 | 100,017 |
| PS1,000,000 | 0.3239 | 1,000,173 |
| PB | 0.2385 | 353,455 |
| PS-0 | 0.0675 | 4,845 |
| PS-1 | 0.1049 | 21,697 |
| PS-2 | 0.1932 | 172,756 |
| PS-3 | 0.2870 | 663,061 |

**TABLE III**
**Thermal Properties of sPS Copolymers Obtained with the Cp*TiCl$_3$/MMAO Catalyst**

| Sample | First heating[a] | | | | | Cooling[a] | | Second heating[a] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $T_g$ (°C) | $T_{m11}$ (°C)[b] | $\Delta H_{11}$ (J/kg) | $T_{m21}$ (°C)[c] | $\Delta H_{21}$ (J/kg) | $T_c$ (°C) | $\Delta H_c$ (J/kg) | $T_g$ (°C) | $T_{m12}$ (°C)[b] | $\Delta H_{12}$ (J/kg) | $T_{m22}$ (°C)[c] | $\Delta H_{22}$ (J/kg) |
| PS-0 | NA | NA | NA | 247 | 22 | 205 | 22 | 100 | NA | NA | 247 | 22 |
| PS-1 | NA | NA | NA | 246 | 15 | 196 | 14 | 99 | NA | NA | 246 | 15 |
| PS-2 | NA | −13 | 1 | 246 | 14 | 196 | 14 | 99 | −20 | 1 | 245 | 14 |
| PS-3 | NA | −12 | 7 | 248 | 7 | 198 | 7 | 99 | −20 | 2 | 246 | 7 |

$\Delta H_{21}$ = heat of second crystalline, melting peak of first heating; $\Delta H_c$ = heat of crystallization; NA = not available; $T_c$ = crystallization temperature.
[a] Determined by DSC at the rate of 20°C/min.
[b] $T_m$ for PB.
[c] $T_m$ for the sPSMS copolymer.

From the $M_w$ results in Table I, we found that PS-3 exhibited the highest $M_w$, which was higher than $M_w$ of PB. On the other hand, the $M_w$ values of PS-1 and PS-2 were lower than that of PB. This might be due to the effect of solvent cage diffusion and the anionic graft reaction initiated first by small-chain PB, which was observed in 0.5 and 1 h; long-chain PB was grafted onto the backbone when the reaction time increased to 2 h. Because of the high molecular weight of the macromolecules, the rate of their diffusion was lower than that of small molecules in liquids.[17] Thus, the reactions of large molecules in the polymers were much lower than those of small molecules, so larger $M_w$ values were clearly observed with longer reaction times.

Table III shows the thermal properties of sPS copolymers as determined by DSC, and examples of DSC curves of poly(sPSMS-g-PB) [PS-3 (2 h)] are shown in Figure 5. Generally, sPS is a semicrystalline material and displays very high melting temperatures ($T_m$'s) up to 270°C.[18] According to Table III, the $T_m$ value of PS-0 was lower than 270°C because when MS units were introduced into the sPS backbone, the quality of the crystals of sPS decreased. The bulkiness or electron-donating effect of the CH$_3$ groups may have prevented the crystallization of sPS.[19] After PB was grafted onto the sPSMS backbone, the $T_m$ values of PS-1, PS-2, and PS-3 remained approximately the same. It can be implied that grafted PB did not significantly interfere with the quality of sPSMS crystals because $T_m$ of sPSMS remained the same.

On the other hand, a comparison of the results for the crystalline melting heat of sPS ($\Delta H_2$) obviously
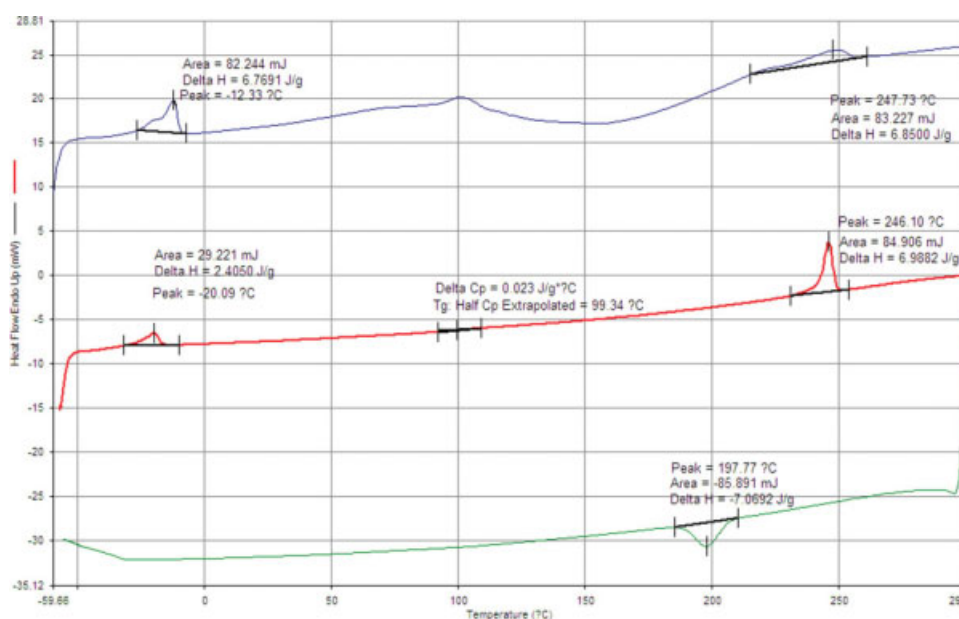


**Figure 5** DSC curves of PS-3 [poly(sPSMS-g-PB); 2-h reaction and 20°C/min]: first heating curve of the fresh copolymer from the reactions (top), second heating curve after the cooling curve (middle), and cooling curve after the first heating curve (bottom). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
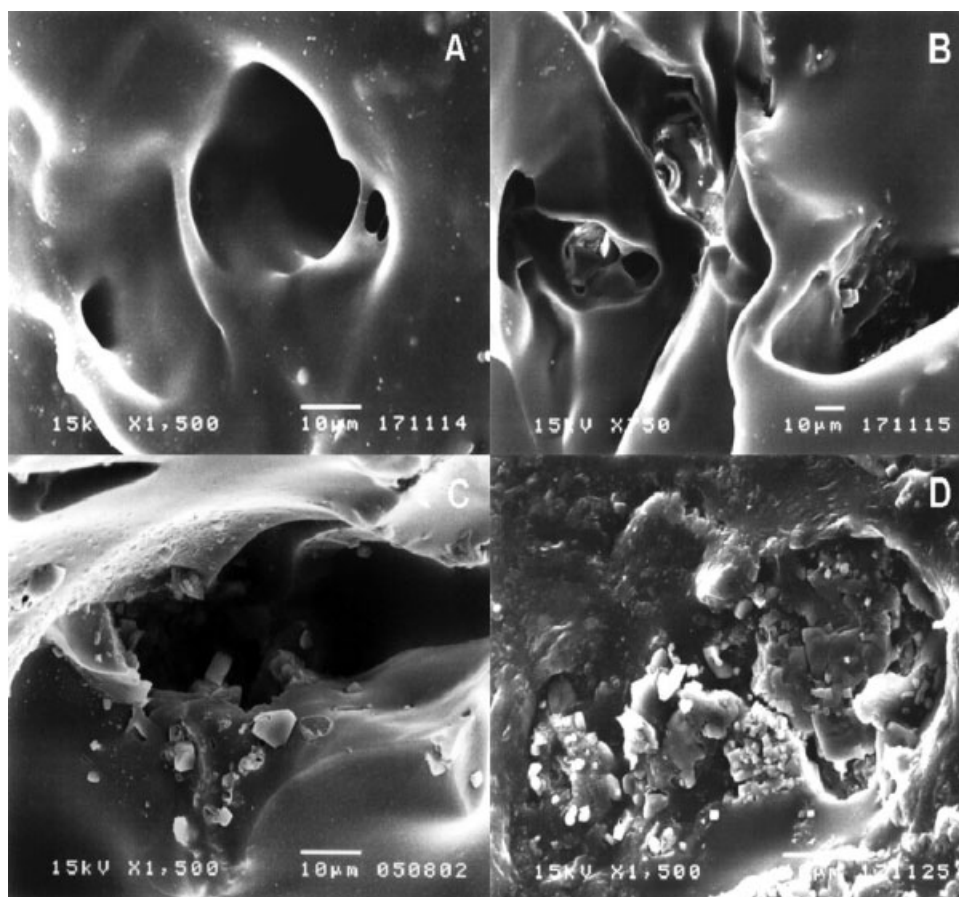
**Figure 6**  SEM micrographs of sPS copolymers: (A) PS-0, (B) PS-1, (C) PS-2, and (D) PS-3.

shows that grafted PB affected the values of $\Delta H_2$ of the graft copolymers. The $\Delta H_2$ value of the copolymer continuously decreased when more PB was grafted onto the sPSMS backbone, implying that the incorporation of the grafted PB tended to interrupt the crystallization quantities of the sPSMS main chain. This was probably due to a bulky group of PB, which could have resulted in steric hindrance. Thus, the packing density of the polymer chains decreased, and this resulted in a decrease in the crystallinity of poly(sPSMS-$g$-PB).[1] The decrease in $\Delta H_2$ of the graft copolymers was not directly proportional to the percentage of PB involved (it increased ca. 3 times in each step). Thus, the decrease in $\Delta H_2$ of the graft copolymers was more likely to happen because of the hindrance from the involved PB chains rather than the decreases in the quantities of crystalline sPSMS. Moreover, the graft copolymers had two $T_m$ values: the first $T_m$ corresponded to high $cis$-PB, and the second $T_m$ corresponded to the crystallinity of sPSMS. Both the decrease in $\Delta H_2$ of sPSMS and the increase in $\Delta H_1$ of the involved high $cis$-PB changed because of the high $cis$-PB presented.

To confirm these results, the surface morphology of sPS copolymers was investigated with SEM, and this is shown in Figure 6.

The graft sPSMS changed both the thermal properties and the surface morphology. It was found that the graft copolymers consisted of two phases. Figure 6 exhibits the distribution of $cis$-PB (rubber particles) into sPSMS (dark phase). When comparing Figure 6(A) and the others, we found that when PB was grafted to the backbone, rubber particles appeared as phases separated from the dark phase. It should be noted that the rubber particles were not simple rubber spheres. Furthermore, the content and distribution of $cis$-PB increased with the reaction time, corresponding to the aforementioned results.

### Blending of poly(sPSMS-$g$-PB)

There have been many attempts to improve the impact resistance of original sPS. Rubber toughening of sPS and poly(styrene/diphenyl–ethylene)[20] and the blending of sPS with poly($p$-phenylene sulfide)[21] have been studied to improve these properties. It is well known that block and graft copolymers are effective compatibilizers in immiscible blends. This study investigated the effect of the synthesized grafting copolymer, poly(sPSMS-$g$-PB), and compared the impact strengths of pure sPS and poly(sPSMS-$g$-PB)/pure sPS blends. Blend samples were prepared by melt mixing
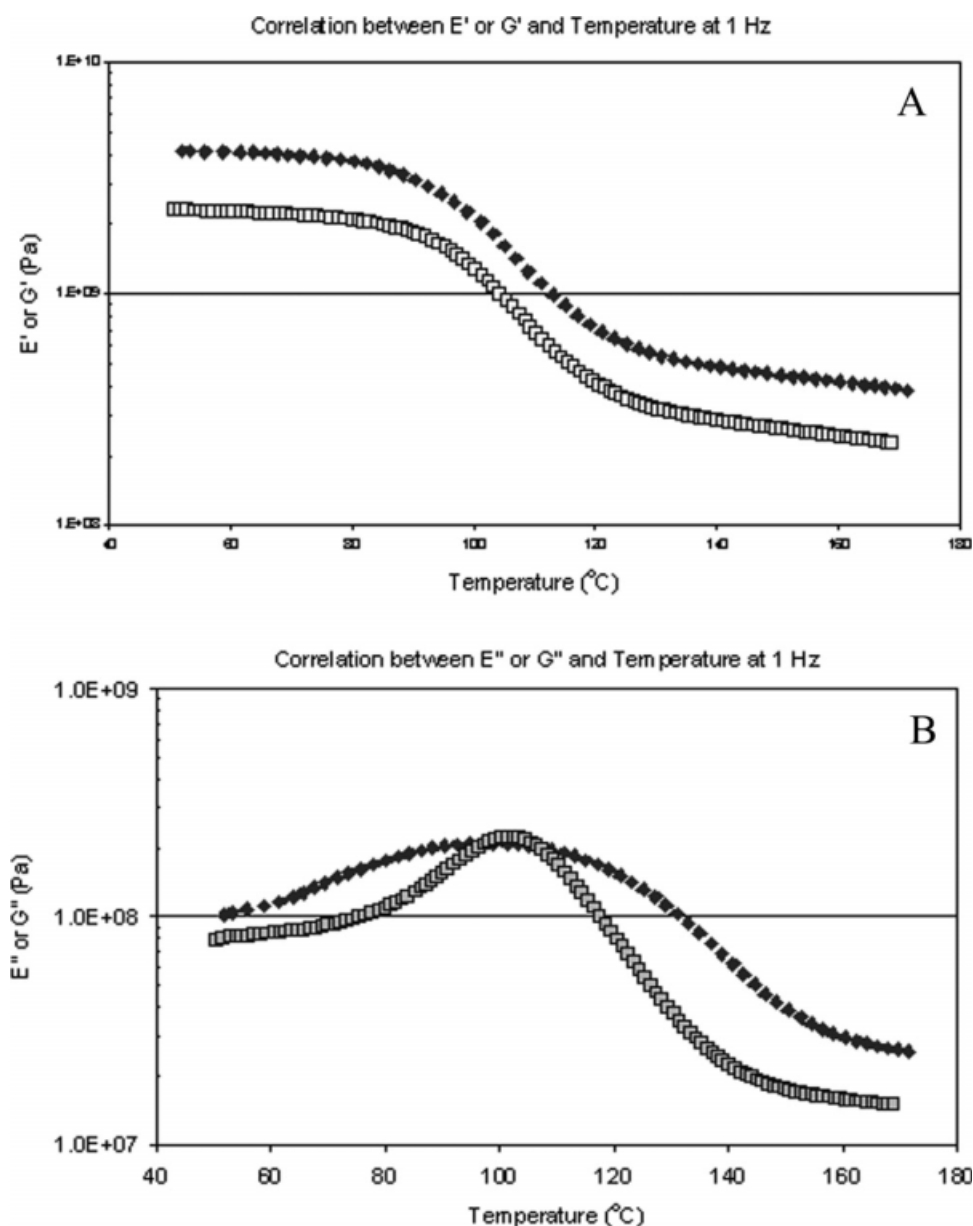
**Figure 7** Dynamic mechanical analysis results for commercial sPS and a poly(sPSMS-*g*-PB) blend with pure sPS: (◆) poly (sPSMS-*g*-PB) blend with pure sPS and (□) pure sPS.

and had 0.25% poly(sPSMS-*g*-PB). The mechanical properties of the pure sPS and poly(sPSMS-*g*-PB)/ pure sPS blend are shown in Figure 7.

As shown in Figure 7(A), the storage modulus ($E'$ or $G'$) of the blends was higher than that of pure sPS, so poly(sPSMS-*g*-PB) could improve the toughness and strength of the original sPS. As shown in Figure 7(B), the loss modulus ($E''$ or $G''$) of the blends also was higher than that of pure sPS, and this indicated that the blend of poly(sPSMS-*g*-PB) could absorb more energy than pure sPS because sPS showed no segmental mobility of chain segments below its $T_g$ and did not exhibit long-range energy dissipation deformation processes on impact below the $T_g$.[2] This is a reason that sPS is very brittle at this temperature. Thus, the addition of poly(sPSMS-*g*-PB) to the rubber phase in the sPS matrix and PB particles can absorb and dissipate energy when the forces or loads interact with samples. It can be concluded that the poly(sPSMS-*g*-PB)/pure sPS blend had slightly better mechanical strength and was less brittle than pure sPS. Moreover, the graft copolymer can be used as an interphase binder in the case of sPS blended with PB; the impact strength of the immiscible blends can obviously be improved.

## CONCLUSIONS

Poly(sPSMS-*g*-PB) with highly syndiotactic PS segments in the backbone and *cis*-PB side chains was

successfully prepared by the combination of metallocene and anionic grafting reaction techniques. It was possible to incorporate the large molecules of unsaturated elastomer PBs into the backbone of sPSMS chains. The microstructures of the butadiene and styrene units were proved to be highly syndiotactic. A high $T_m$ value (240–250°C) was shown, and it was different from those of normal anionic styrene–butadiene copolymers because of the presence of crystalline sPS segments. The grafted PB content increased with the reaction time, and these grafting reaction systems represented the effects of solvent cages. The quantity of sPS crystals decreased when PB was grafted onto the sPSMS backbone. The poly (sPSMS-$g$-PB)/pure sPS blend had higher strength and toughness than pure sPS, and this was confirmed by dynamic mechanical analysis results. Therefore, poly(sPSMS-$g$-PB) might be used as a compatibilizer in sPS blends to modify their mechanical properties.

## References

1. Li, C. L.; Chan, S. H.; Ting, C.; Jiang, G. J. J Appl Polym Sci 2002, 86, 1038.

2. Scheirs, J.; Priddy, D. B. Modern Styrenic Polymers: Polystyrene and Styrenic Copolymers; Wiley: Chichester, England, 1999.

3. Liu, S.; Huang, B. Macromol Rapid Commun, 1999, 20, 484.

4. Endo, K.; Senoo, K. Polym Bull 2000, 44, 25.

5. Xu, G.; Chung, T. C. Macromolecules 1999, 32, 8689.

6. Kobayashi, E.; Kaita, S.; Aoshima, S.; Furakawa, J. J Polym Sci Part A: Polym Chem 1994, 33, 2175.

7. Kobayashi, E.; Hayashi, N.; Aoshima, S.; Furakawa, J. J Polym Sci Part A: Polym Chem 1998, 36, 1707.

8. Endo, K.; Matsuda, Y. J Polym Sci Part A: Polym Chem 1999, 37, 3838.

9. Caprio, M.; Serra, M. C.; Bowen, D. E.; Grassi, A. Macromolecules 2002, 35, 9315.

10. Senoo, K.; Endo, K.; Tosaka, M.; Murakami, S.; Kohjiya, S. Macromolecules 2001, 34, 1267.

11. Endo, K.; Senoo, K. Macromol Rapid Commun 1998, 19, 536.

12. Ban, H. T.; Tsunogae, Y.; Shiono, T. J Polym Sci Part A: Polym Chem 2004, 42, 2698.

13. Ban, H. T.; Tsunogae, Y.; Shiono, T. J Polym Sci Part A: Polym Chem 2005, 43, 1188.

14. Zheng, G.; Stöver, H. D. H. Macromolecules 2002, 35, 6828.

15. Chung, T. C.; Lu, H. L.; Ding, R. D. Macromolecules 1997, 30, 1272.

16. Billmeyer, F. W., Jr. Textbook of Polymer Science, 3rd ed.; Wiley: Singapore, 1984.

17. Denisova, E. T.; Denisova, T. G.; Pokidova, T. S. Handbook of Free Radical Initiators; Wiley: Hoboken, NJ, 2003; p 29.

18. Ishihara, N.; Kuramoto, M.; Uoi, M. Macromolecules 1988, 21, 3356.

19. Nakatani, H.; Nitta, K.-H.; Soga, K.; Tanaka, T. Polymer 1997, 38, 4751.

20. Ramsteiner, F.; McKee, G. E.; Heckmann, W.; Oeepen, S.; Geprägs, M. Polymer 2000, 41, 6635.

21. Hwang, S.-O.; Kim, M.-J.; Jung, J.-C. Eur Polym J 2002, 38, 1881.