

Graft Copolymerization of Styrene or Methyl Methacrylate onto Syndiotactic Polystyrene by ATRP Technique

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ABSTRACT: Functionalized syndiotactic polystyrene (sPS) copolymers, including sPS-*graft*-atactic polystyrene (aPS) copolymer or sPS-*graft*-poly(methyl methacrylate) (PMMA) copolymer, were synthesized and characterized. sPS has been synthesized by using half sandwich titanocene/methylaluminumoxane catalyst in homogenous conditions. Then, α -phenyl chloroacetylation of sPS was accomplished in a heterogeneous process by using carbon disulfide as dispersing medium and α -phenyl chloroacetyl chloride and anhydrous aluminum chloride as acetylating agent and catalyst, respectively. The graft copolymer of sPS with aPS

or PMMA were synthesized by atom transfer radical polymerization using α -phenyl chloroacetylated sPS as initiator and CuBr and bipyridine as catalyst. The structure of obtained copolymer was investigated by ^1H NMR, FTIR spectroscopy, and thermal behavior of copolymers was performed by differential scanning calorimetry analyses. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 611–619, 2007

Key words: syndiotactic polystyrene; metallocene catalyst; graft copolymer; ATRP; living radical polymerization

INTRODUCTION

Syndiotactic polystyrene (sPS) has been prepared by half sandwich metallocene catalysts activated by methylaluminumoxane (MAO). Because of its stereoregularity, sPS is crystalline with a melting point greater than 270°C. This, along with its good chemical resistance, low water absorbability, and enhanced mechanical properties, makes sPS an attractive engineering thermoplastic with versatile application in many fields, such as the automotive, electronic, and packaging industries. Thus, sPS exhibits not only good chemical resistance but enhanced mechanical performance at elevated temperatures as well.^{1–5}

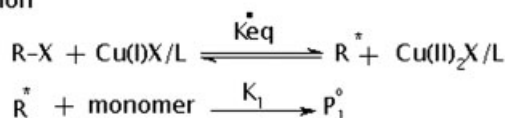
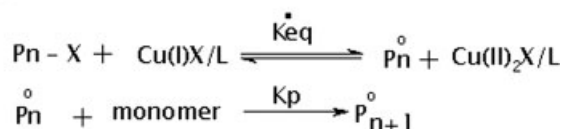
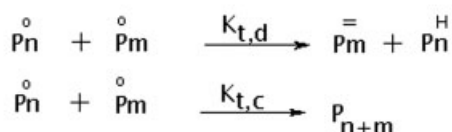
However, its inherent brittleness and poor impact and tear resistance significantly limit some end uses. Recently, several attempts have been made to improve the physical properties and processability of sPS through several procedures. One involves syndiotactic copolymerization of styrene with a second monomer, especially ethylene, to produce a styrene/olefin copolymer.⁶ Another modification procedure involves the preparation of functionalized sPS, such as sulfonated sPS,⁷ acetylated sPS,⁸ maleic anhydride grafted sPS,⁹ and hydroxylated sPS.¹⁰ Physical blending with other polymers is a versatile and economical possibility for producing a material that combines

properties of the two blended polymers.^{11–14} Indeed, blending with elastomers and fibers may extend the commercial utility of sPS.^{15,16} However, since sPS lacks functionalities capable of interacting with the second polymer, blending sPS with other polymers usually leads to phase separation. This problem can be solved with new graft or block compatibilizers the incorporate sPS and the second polymeric component. The graft or functionalized sPS may be the first choice to serve as compatibilizer. It has been a scientific challenge and industrially interesting subject to prepare graft copolymers having stereoregularity on the main chain. Endo et al. reported the synthesis of syndiotactic graft copolymers of sPS-*graft*-atactic polystyrene (aPS) via syndiospecific copolymerization of styrene with styrene macromonomer bearing terminal styryl group by CpTiCl₃-MAO catalyst.¹⁶ Liu and Sen reported the synthesis of sPS graft copolymers by atom transfer radical polymerization (ATRP) using brominated sPS as an organic halide initiator.¹⁸

ATRP catalyzed by transition metal (such as copper, ruthenium, nickel, etc) halide complexes with 2,2'-bipyridine (bpy) derivatives for polymerization of various monomers, such as styrene, methacrylates, acrylates, etc., has been developed in our laboratory and other laboratories.^{19–21}

ATRP employs equilibrium between dormant alkyl halides and active propagating radicals, to maintain a low concentration of active species. The activated radical species can either propagate or be deactivated to reform the dormant species (Scheme 1). ATRP also has an advantage in utilizing a wide range of initia-

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Initiation**Propagation****Termination**

Scheme 1 Mechanism of atom transfer radical polymerization.

tors. Alkyl halides with radical stabilizing substituents such as carbonyl, cyano, or aryl group adjacent to the C—X can be used as initiator. Any compound, including macromolecular species, can potentially be used to initiate ATRP as long as they contain activated halogen atoms.

The present work is designed to synthesize sPS and sPS-*graft* copolymers by utilizing the ATRP of methacrylates monomers (e.g., MMA) or aPS from α -phenyl chloroacetylated sPS (α -ph-ch-sPS) macroinitiator. The partially α -ph-ch-sPS macroinitiator was prepared from the acid-catalyzed halogenation reaction of sPS, which was synthesized in a heterogeneous process with α -phenyl chloroacetyl chloride and anhydrous aluminum chloride in carbon disulfide via Friedel–Crafts acylation reaction.

EXPERIMENTAL

Instrumentation

^1H NMR spectra were obtained at 25°C on FT-NMR (400 MHz) Bruker spectrometer. Sample for ^1H NMR spectroscopy was prepared by dissolving about 10 mg of products in 5 mL of deuterated chloroform. FTIR spectra were recorded using Shimadzu FTIR-8101M.

Differential scanning calorimetry (DSC) analyses were performed on a Mettler 4000 TA thermal analytical system.

Materials

Styrene (Tabriz Petrochemical Company) was vacuum distilled from CaH_2 and stored under N_2 . 2,2'-Bipyridine (bpy) was used without purification. Cuprous chloride, toluene, and anisole were purchased

from Merck and purified and dried by conventional methods before use.²² Indene (90%, Merck) was purified by vacuum distillation. Titanium tetrachloride (TiCl_4 , 8%, Merck), *n*-butyllithium (*n*-BuLi, reagent grade in hexane solution; Merck), methylaluminumoxane, 10% in toluene (Aldrich) were used without further purification.

All other chemicals were purchased from Merck and used without further purification. Aluminum trichloride was purchased from Aldrich.

Synthesis of 1-methylindene

A suspension of 10.0 g (0.082 mol) of indenyllithium in 250 mL of hexane contained in a 500 mL side-armed flask fitted with an overpressure bubbler was chilled to 0°C. Iodomethane (5.1 mL, 0.082 mol) was added dropwise via syringe to the flask and the mixture was allowed to stir overnight at room temperature. The solution was filtered and the hexane removed under vacuum to yield 9.1 g (86%) of a yellow oil. The product was distilled at 30°C/29 in. Hg and colorless oil was obtained which turned yellow on standing at room temperature. ^1H NMR (CDCl_3): δ 7.4–7.0 (m, 4H, arom), 6.77 (dd, 1H, sp^2 3-position), 6.46 (dd, 1H, sp^2 2-position), 3.50 (q of t, 1H, sp^3 1-position), 1.30 (d, 3H).

Synthesis of 1-trimethylsilyl-3-methylindene

1-Methylindene (5.0 g, 0.038 mol) was dissolved in 100 mL of hexane containing in a 250 mL side-armed flask fitted with a gas inlet connected to an overpressure bubbler. To this solution, 24.1 mL of 1.6M *n*-butyllithium (0.038 mol) was added dropwise and the mixture was stirred overnight at room temperature. The supernatant liquid was decanted and the white precipitate was washed with three 100 mL portions of hexane. Fresh distilled hexane (100 mL) was introduced to the flask, 5.5 mL (0.043 mol) of chlorotrimethylsilane was added dropwise via a syringe to the stirred suspension, and the mixture was allowed to stir overnight. The solution was then filtered and the solvent removed under vacuum, leaving 6.52 g (85%) of a yellow oil. The crude product was further purified via distillation at 45–47°C/29 in. Hg to yield a colorless oil which darkened on standing at room temperature. ^1H NMR (CDCl_3): δ 7.55–7.11 (m, 4H, arom), 6.35 (m, 1H, sp^2 2-position), 3.40 (m, 1H, sp^3 1-position), 2.28 (dd, 3H, CH_3 3-position), 0.00 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

Synthesis of 1-methylindenyltrichlorotitanium

The method of preparation was the same as that for indenyltrichlorotitanium except that 5.42 g (0.027 mol) of 1-trimethylsilyl-3-methylindene was added to 3.2 mL (0.027 mol) of TiCl_4 . The dark-red crystalline

product was obtained in 94% yield (7.17 g). ^1H NMR (CDCl_3): δ 7.80–7.33 (m, 2H, arom), 7.60 (m, 2H, arom), 7.13 (d, 1H 3-position), 6.93 (d, 1H, 2-position), 2.76 (s, 3H, CH_3).

Synthesis of sPS

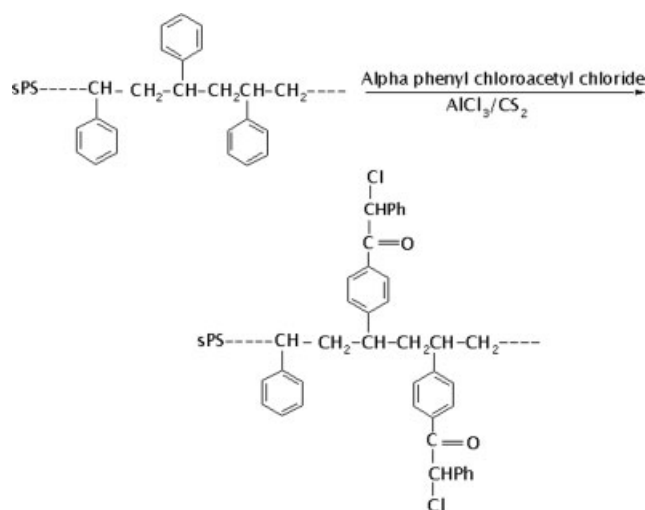
The styrene polymerization was performed by injecting the 30 mL of toluene, followed by injection of 5.0 mL of styrene (previously dried over CaH_2 for 12 h and distilled from CaH_2), followed by injection of 3.2 mL of 3.1M MAO, into 100 mL crown-capped pressure bottles sealed under inert atmosphere and brought to constant at 50°C . At this time the solution was stirred for 10 min to scavenge impurities. Polymerization was initiated by injection of 0.5 mL of 5 mM titanium precursor solution. Polymerization reaction was run for 30 min and quenched by the addition of 100 mL of 10% HCl-methanol. The resulting polymer was filtered, dried, and weighed (for calculation of activity). The bulk polymer was extracted using a Soxhlet extractor for 12 h in 2-butanone, dried, and weighed (for calculation of percentage sPS). The syndiotactic index of obtained polymer is more than 91%.

α -Phenyl-chloroacetylation of sPS

Acetylation reaction was performed in a heterogeneous process. 0.6 g of sPS was suspended in 40 mL of CS_2 in a two-necked, round-bottom flask fitted with a condenser and CaCl_2 guard tube. The reaction system was maintained at 20°C and was stirred vigorously with a magnetic pellet. Then 2.0 g of AlCl_3 (0.015 mol) was added rapidly. After the mixture turned into orange-red in color, α -phenyl chloroacetyl chloride 2.2 mL (0.015 mol) was added through a dropping funnel after dilution with 20 mL CS_2 . The reaction was conducted at 20°C for 3 h and then terminated by addition of the ice water followed by concentrated hydrochloric acid (Scheme 2). The polymer was filtered, washed several times with distilled water, and dried under vacuum at 70°C . Yield: 1.05 g (white powder). FTIR (KBr, cm^{-1}): 3053 (phenyl protons of α -phenyl-chloroacetyl chloride and sPS), 2951 (aliphatic protons of α -phenyl-chloroacetyl chloride and sPS), 1729 ($-\text{CO}-$ group of α -phenyl-chloroacetyl chloride), 1311 ($[\text{s}]\text{bondPhCH Cl}$ groups of α -phenyl-chloroacetyl chloride).

Synthesis of sPS-graft-PMMA and sPS-graft-aPS

In a typical experiment, a dry round-bottomed flask fitted with magnetic stirring bar was charged with anisole (15 mL), CuBr (0.07 g, 0.48 mmol), bpy (0.15 g, 0.96 mmol), MMA (3 mL, 28 mmol), and α -ph-ch-sPS (0.2 g). The flask was sealed and three cycles of



Scheme 2 α -phenyl chloroacetylation of sPS.

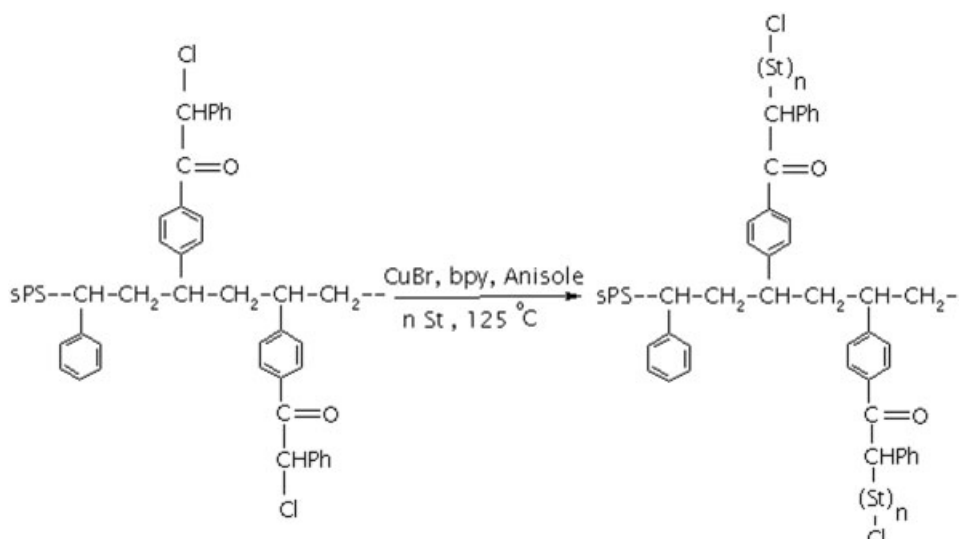
freeze-pump-thaw were performed to remove oxygen. Then the flask was filled with purified nitrogen. After which the reaction mixture was heated at 90°C and maintained at this temperature for 10 h with stirring. The reaction was terminated by pouring the content of the flask into a large amount of acidic methanol. The precipitated polymer was filtered, washed several times, and dried under vacuum. For synthesis of sPS-graft-aPS, the above procedure was used except styrene was the monomer and the reaction temperature was 125°C (Schemes 3 and 4). The obtained powders (sPS-graft-poly(methyl methacrylate) (PMMA) or sPS-graft-aPS) were extracted with cyclohexane at 30°C for three times, to remove polystyrene and polymethyl methacrylate homopolymers.

RESULTS AND DISCUSSION

Synthesis of catalyst precursors and polymerization results

1-Substituted alkylindenes was prepared in 85% yields. In the case of methyl, ethyl, and *tert*-butylindenes, the specific 1- or 3-isomer isolated were found to be solvent mediated. The substituted inden was converted into trimethylsilyl derivative via reaction of intermediated organolithium analogue with chlorotrimethylsilane. The corresponding titanium complex was synthesized in excellent yield via reaction of the trimethylsilylindene derivative with TiCl_4 , using procedure described for analogous cyclopentadienyl-titanium complexes.²³ The titanium complex was evaluated as styrene polymerization catalyst in toluene solution when activated by methylaluminumoxane.²⁴

The present results demonstrate the importance of both electronic and steric effects in styrene polymerization promoted by alkyl-substituted indenyltrichlorotitanium compounds when activated by MAO. The



Scheme 3 Graft copolymerization of syndiotactic PS with atactic PS.

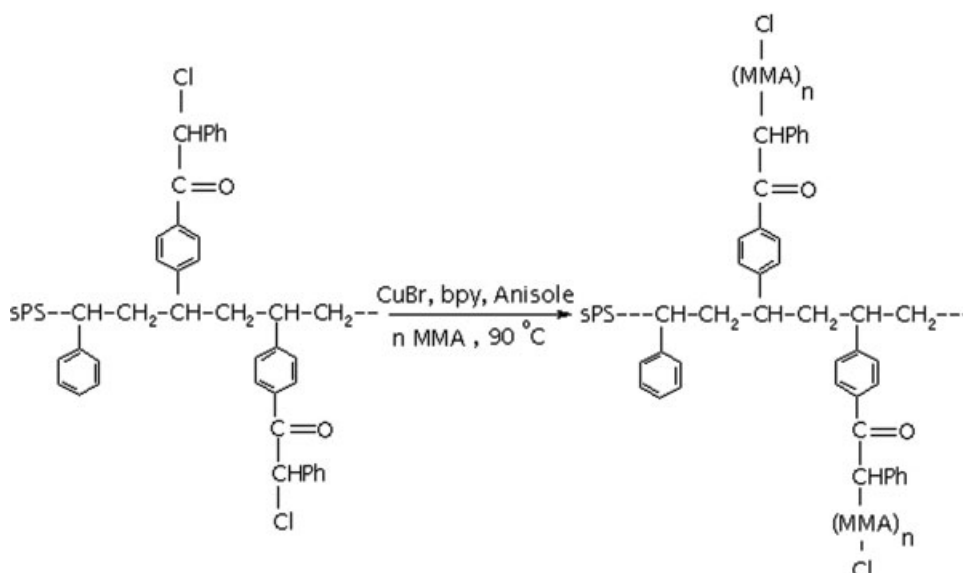
increase in activities of $\text{Cp} < \text{Ind} < 1\text{-(Me) Ind}$ complexes is consistent with the concept that electron-releasing alkyl groups enhance the activity at the electrophilic metal center, and in general, increase the syndiospecificity as well.²⁵

α -Phenyl-chloroacetylation of sPS

Friedel–Crafts acylation reactions are aromatic substitution reaction in which benzene (or a substituted benzene) undergoes acylation when treated with carboxylic acid derivatives (usually acyl halide or anhydride) and a Lewis acid catalyst, such as aluminum chloride. The carbonyl group in such acid derivatives is sufficiently basic that formation of a carbonium ion

complex occurs with a strong Lewis acid, and in many cases the complex itself is sufficiently electrophilic to react with aromatic rings.²⁶ Recently, the Friedel–Crafts acylation reaction was used by Sun et al.^{27,28} and our research group^{29,30} to prepare acetylated aPS and to prepare acetylation of polyvinyl chloride in mild condition, respectively.

In this work, the α -ph-ch-sPS was synthesized in a heterogeneous process through Friedel–Crafts chloroacetylation reaction. Powder sPS was partially chloroacetylated using α -phenyl-chloroacetyl chloride as chloroacetylated agent and aluminum chloride as catalyst in carbon disulfide (Scheme 2). The final product of chloroacetylation reaction is an aromatic ketone.



Scheme 4 Graft copolymerization of syndiotactic PS with methyl methacrylate.

We characterized the resulting ring- α -ph-ch-sPS by DSC, FTIR, and ^1H NMR spectroscopy. FTIR spectra for the starting sPS and the α -ph-ch-sPS product are shown in Figures 1(A) and 1(B).

The FTIR spectra of α -ph-ch-sPS exhibits a sharp absorption band at 1729 cm^{-1} attributed to carbonyl stretching bond and absorption band at 1311 cm^{-1} attributed to $-\text{CHCl}$ in $-\text{OCHClPh}-$ bending bond.

Figures 2(A, B) shows the ^1H NMR spectra of α -ph-ch-sPS from Friedel-Crafts acylation of sPS. It is obvious that the signal peak at $\delta = 3.95\text{ ppm}$ could be attributed to α -phenyl-chloroacetyl protons ($\text{Ph}-\text{CH}$), and the peak at $\delta = 7.6\text{ ppm}$ could be attributed to the α aromatic protons of chloroacetyl group, respectively.³¹

The DS (degree of substitution) content of α -ph-ch-sPS was determined by ^1H NMR, using the intensity of aliphatic protons ($x =$ aliphatic protons of α -ph-ch-sPS and $y =$ aliphatic protons of unsubstituted sPS according to Fig. 2) versus methene protons of α -ph-ch-sPS. DS can be calculated by eq. (1)

$$\begin{aligned} 3x + 3y &= m & (1) \\ x &= n \\ \text{D.S} &= 4.23\% \end{aligned}$$

where m is the intensity of aliphatic protons and n is the intensity of proton of α -ph-ch-sPS [Fig. 2(B)].

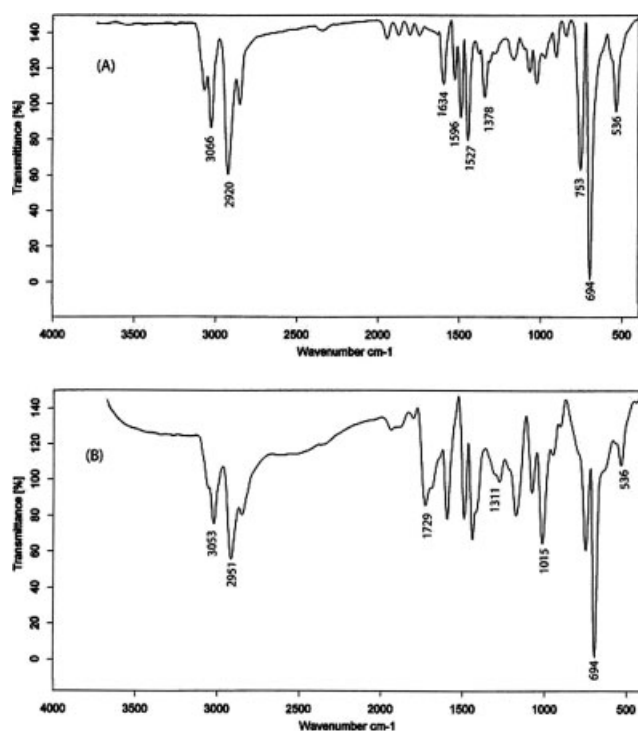


Figure 1 (A) FTIR spectrum of sPS and (B) FTIR spectrum of the α -phenyl-chloroacetylated sPS.

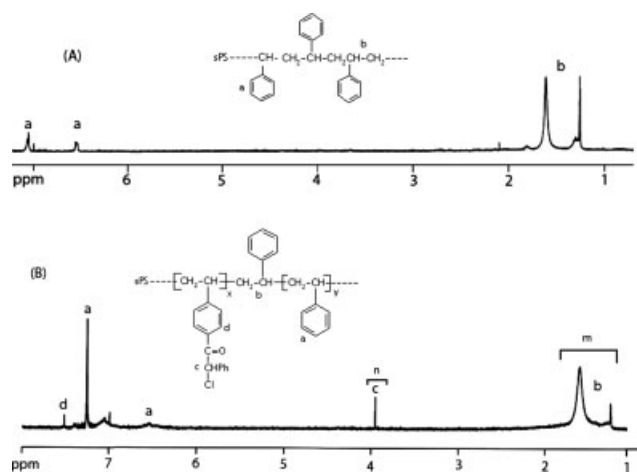


Figure 2 (A) ^1H NMR spectrum sPS and (B) ^1H NMR spectrum of the α -phenyl-chloroacetylated sPS.

According to ^1H NMR spectrum [Fig. 2(B)], it is possible to calculate DS via the following simple eq. (2):

$$\text{D.S} = 3n/m = 4.23\% \quad (2)$$

Additional evidence on the effectiveness of the α -phenyl chloro acetylation reaction onto sPS was also obtained from the DSC data. In DSC curves of α -ph-ch-sPS no T_m and T_c were detected, which indicated that the sample was unable to crystallize. In α -ph-ch-sPS, because of the large size of the substituent group, the α -ph-ch-sPS unit exists only in the amorphous region. The α -ph-ch-sPS can be treated as statistical copolymer with a crystallizable component of syndiotactic styrene units and noncrystallizable α -ph-ch-styrene units.³²

Synthesis of sPS-graft-PMMA and sPS-graft-aPS

Organic halides ($\text{R}-\text{X}$) efficiently initiate ATRP in the presence of certain transition metal complexes, M_t^n . In this polymerization, dormant polymer halide, $\text{R}-(\text{monomer})_n-\text{X}$, is repeatedly activated by the transition metal compound to produce the growing radical, $\text{R}-(\text{monomer})_n^\bullet$, and the oxidized transition metal species, M_t^{n+1} . The equilibrium between dormant and growing species is fast and reversible. The low concentration of radicals minimizes termination relative to propagation rate, and a controlled/living polymerization is achieved³³ (Scheme 1).

In this work, sPS was partially α -phenyl chloroacetylated at the benzylic positions using α -phenyl-chloroacetyl chloride as chloroacetylated agent and aluminum chloride as catalyst in carbon disulfide. The α -ph-ch-sPS was used as an organic halide initiator in the presence of CuBr combined with the ligand 2,2'-bpy, as the catalyst, to graft PMMA or aPS. The over-

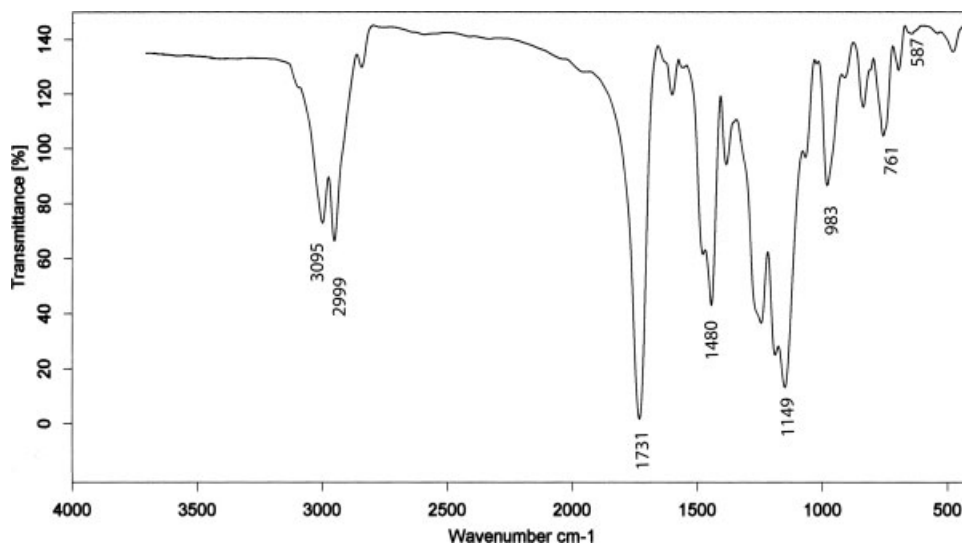


Figure 3 FTIR spectrum of syndiotactic polystyrene-*graft*-polymethyl methacrylate.

all procedure is summarized in Schemes 3(A) and 3(B). As mentioned previously, α -haloketones are among the best initiators for the ATRP of MMA and styrene. The stronger electron-withdraw power of the ketone's carbonyl induces further polarization of carbon-halogen bond, which leads to fast initiation. However, benzyl-substituted halides fail in the polymerization of more reactive monomers in ATRP such as MMA, though they are useful initiator for the polymerization of styrene due to their structural resem-

blance. In this regards, α -ph-ch-sPS is a more efficient initiator for the ATRP of styrene and methacrylate than the method that was reported previously.¹⁸

The graft copolymer of MMA initiated by the α -ph-ch-sPS as macroinitiator in the presence of CuCl/bpy catalyst system was analyzed by FTIR (Fig. 3) and ¹H NMR spectroscopy (Fig. 4). In FTIR spectroscopy, the spectrum of the graft copolymer displays a typical carbonyl stretch (1731 cm⁻¹), which is related to the carbonyl groups of the PMMA segments.

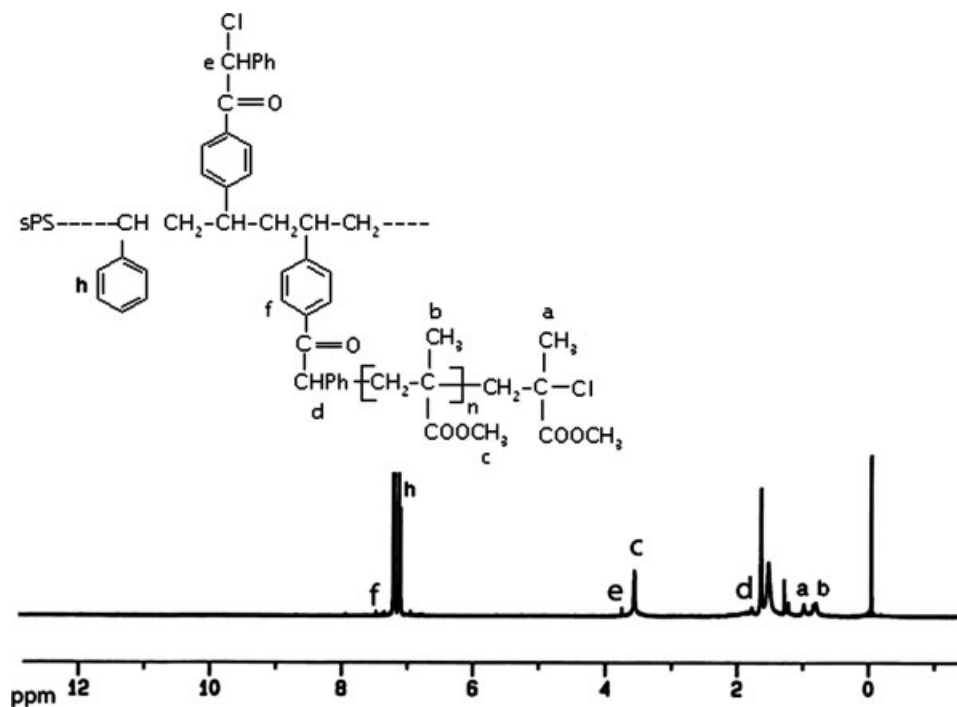


Figure 4 ¹H NMR spectrum of syndiotactic polystyrene-*graft*-polymethyl methacrylate.

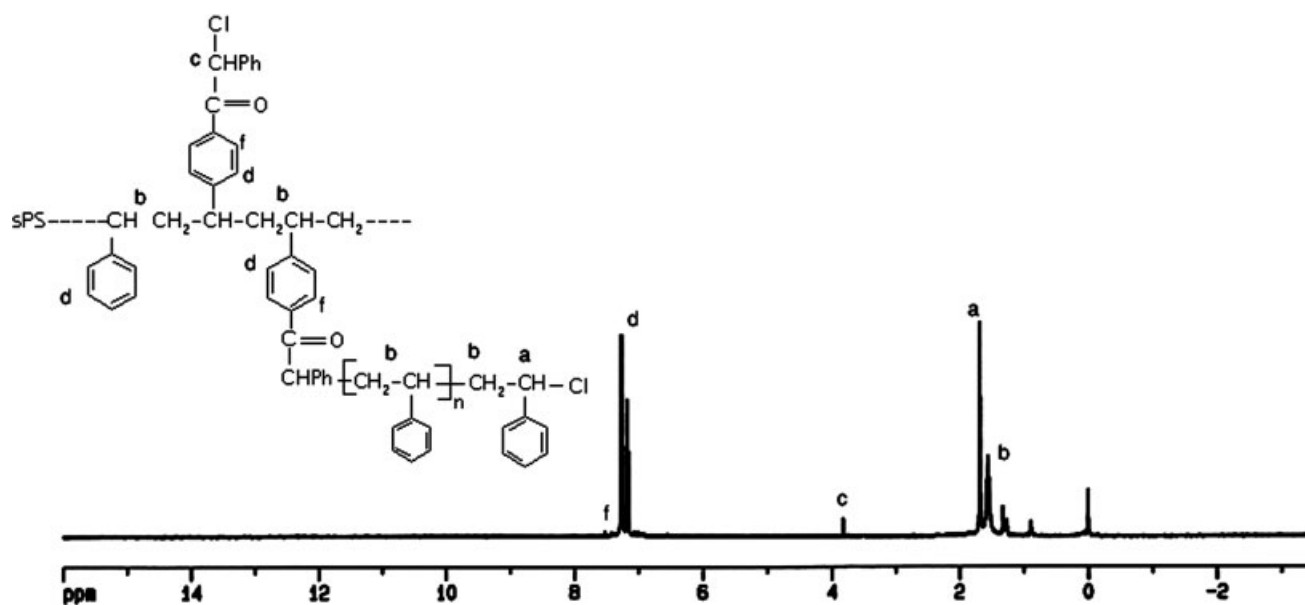


Figure 5 ^1H NMR spectrum of syndiotactic polystyrene-*graft*-atactic polystyrene.

It is obvious that the peak at 587 cm^{-1} could be attributed to $-\text{OCHClPh}-$ in the end of PMMA and it indicates that the polymerization is living.³¹

The ^1H NMR spectrum of PS-*g*-PMMA is illustrated in Figure 4. The spectrum of PS-*g*-PMMA displays a characteristic peak at $\delta = 3.61\text{ ppm}$, which is related to the $-\text{OOCH}_3$ groups of the PMMA segments, and a peak at $\delta = 0.8\text{--}1.1\text{ ppm}$, which is related to the $-\text{CH}_3$ groups of the PMMA according to the NMR spectrum. The related intensity of the chloroacetyl groups of the chloroacetylated sPS macroinitiator showed the formation of grafted copolymer (sPS-*g*-PMMA).

The ^1H NMR spectrum of sPS-*g*-aPS is illustrated in Figure 5. The spectrum of sPS-*g*-aPS displays a characteristic peak at $\delta = 3.81\text{ ppm}$, which is related to the $-\text{CHPhCl}$ groups of the α -ph-ch-sPS, and a peak at $\delta = 0.81\text{--}1.67\text{ ppm}$, which is related to the aliphatic protons of polystyrene and peaks at $\delta = 6.5\text{--}8\text{ ppm}$, which is related to the aromatic protons of polystyrene.

Additional evidence on the effectiveness of the graft copolymerization was also obtained from the DSC data. The graft copolymer studied in this work consists of sPS backbone carrying amorphous PMMA. The presence of the graft segments should affect the melting behavior of the sPS backbone.

The random incorporation of noncrystallizable monomer units into the backbone of a semicrystalline polymer has a marked effect on the thermodynamics and kinetics of crystallization. Relative to behavior observed with homopolymer, crystallizable copolymer usually exhibit low melting temperature, low degree of crystallinity, and a significant decrease in

the overall rate of crystallization.²⁵ The melting behavior of polymers depend on the graft density of polymers.¹⁷ sPS-*g*-PMMA and aPS-*g*-aPS showed lower melting temperature (217 and 219°C) than that of sPS (270°C) [Fig. 6(A–C)].

The T_g data also help in understanding the effects of substituent groups on the movement of polymer chains. It is clear from Figure 6 that the T_g values of the modified polymers depend on the graft copolymerization. This is easy to understand because the substituent groups result in reducing the mobility of the polymer chain and therefore increases the T_g values.

CONCLUSIONS

We have described the efficient synthesis of sPS graft copolymer, sPS-*g*-aPS and sPS-*g*-PMMA by ATRP technique. The grafting was performed using α -ph-ch-sPS as initiator and CuBr combined with bpy as catalyst. α -Phenyl chloroacetylation of sPS was accomplished in a heterogeneous process by using carbon disulfide as dispersing medium and α -phenyl chloroacetyl chloride and anhydrous aluminum chloride as acetylating agent and catalyst, respectively. The ATRP mechanism for grafting was supported by NMR, FTIR, and DSC analysis of end groups. This method of preparation of sPS graft copolymers is attractive because of the relatively wide scope of monomers that can be employed, the stability of catalyst, the simple polymerization procedure, and the good control of graft structure.

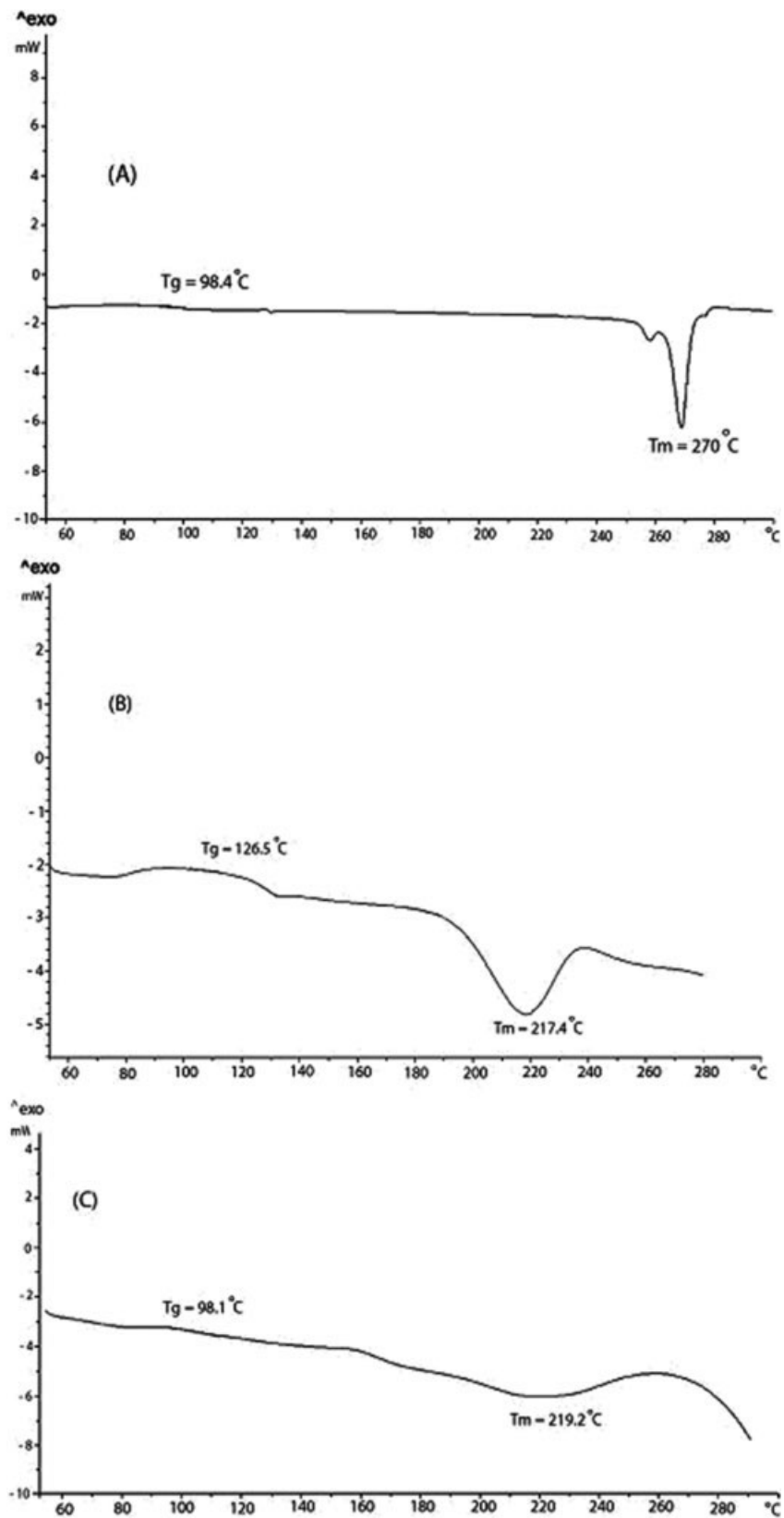


Figure 6 DSC thermogram of (A) syndiotactic polystyrene, (B) syndiotactic polystyrene-graft-polymethyl methacrylate, and (C) syndiotactic polystyrene-graft-atactic polystyrene.

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