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NITROXIDE MEDIATED AND ATOM TRANSFER RADICAL GRAFT POLYMERIZATION OF ATACTIC POLYMERS ONTO SYNDIOTACTIC POLYSTYRENE

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Abstract - ‘Living’ radical graft polymerization was employed to prepare graft copolymers with nitroxide-mediated arylated syndiotactic polystyrene as the backbone and polystyrene (PS), poly(p-methylstyrene) (PMS) and poly(methylmethacrylate) (PMMA) as branches. A two-stage process has been developed to synthesize the macroinitiator. First, syndiotactic polystyrene (sPS) was modified by the Friedel–Crafts reaction to introduce chlorine; second, the chlorine groups were converted to nitroxide mediated groups by coupling with 1-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO-OH). The resulting macroinitiator (sPS-TEMPO) for ‘living’ free radical polymerization was then heated in the presence of styrene and p-methylstyrene to form graft and block copolymers. We used the obtained copolymer and N-bromosuccinimide as brominating agent to achieve polymers with bromine groups. This brominated copolymer was used as a macroinitiator for polymerizing methyl methacrylate in the presence of the CuBr/bpy catalyst system. The formation of the graft and block copolymers was confirmed by DSC, ^{1}H NMR and FTIR spectroscopy. This approach using macroinitiators is an effective method for the preparation of new materials.

Keywords: Syndiotactic polystyrene; Graft copolymer; Poly(methyl methacrylate); Atom transfer radical polymerization; Nitroxide-mediated ‘living’ free radical polymerization; TEMPO.

INTRODUCTION

Syndiotactic polystyrene (sPS) can be prepared by a homogeneous organometallic catalytic system based on a titanium compound and methylaluminoxane (MAO) (Ishihara *et al*., 1986)]Owing to its high melting point (270°C), rapid crystallization rate, low density, excellent chemical resistance and enhanced mechanical properties, sPS has versatile applications in many fields, such as THE automotive, electronic and packaging industries. However, sPS is similar to atactic polystyrene in having poor impact and tear resistance and a low surface energy. The absence of polar groups in this polymer restricts its end uses, especially where adhesion to substrates and compatibility with polar polymers are desired. Therefore, modification of sPS is of interest.

In the past few years, there has been increased emphasis on applications of graft polymers, since they can combine the chemical and physical properties of two or more different monomers into a single polymeric chain. (Brownell *et al*., 2009; Nathinee Srinate *et al*., 2009; Endo *et al*., 2004; Mohajery *et al*., 2008; Can *et al*., 2010). In general,

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*To whom correspondence should be addressed graft polymers can be synthesized by free radical-induced grafting processes, which are the easiest and most widely accepted procedures for the preparation of these kinds of polymers.

Radical polymerization occupies an important position in commercial polymer production because of the scope of applicable monomers, the functional group tolerance, the wide range of reaction conditions, and the lower relative infrastructure costs. Unfortunately, these conventional reactions have significant limitations with respect to a chemist's ability to control the molecular weight distribution, molecular architecture, and composition of the polymers. In order to exact this control, several methodologies have been developed which reduce radical concentrations and efficiently exchange dormant chains with reactive radical species in order to minimize bimolecular termination reactions. The nature of the dormant chain differentiates these processes, with nitroxide-mediated radical polymerization (NMP) (Hawker *et al*., 2001; Moad *et al*., 2008; Shoaeifar *et al*., 2007) exploiting the reversible cleavage of a nitroxide - carbon bond, thiocarbamates supporting a reversible addition - fragmentation chain transfer (RAFT) [Moad *et al*. (2005)] pathway, and ruthenium and copper complexes mediating the exchange of halogen-capped polymer chains through an atom transfer radical polymerization (ATRP) (Matyjaszewski and Xia, 2001; Ouchi *et al*., 2008; Abbasian *et al*., 2006; Gheybi *et al*., 2007; Schellenberg, 2009; Srinate *et al*., 2009; Abbasian *et al*., 2007). Together, these processes are termed controlled radical polymerization (CRP) and provide extraordinary control over polymer molecular weight and molecular weight distributions. Great interest has been placed on the development of CRP mediated by transition metals due to the inherent tunability of metal complexes through alteration of the ligand framework and the flexibility of metal oxidation states in supporting one-electron transformations (di Lena and Matyjaszewski, 2009; Poli and Eur, 2011).

Graft copolymerization of vinyl monomers onto plastics in homogeneous media is one way to modify and enlarge the range of useful plastics. Compared with other graft copolymerizations such as anionic polymerization, an advantage of 'living' free radical polymerization (LFRP) is that, in the preparation of grafted copolymers, the terminal groups are stable in air at room temperature, and prepolymers can be isolated, stored, and used as needed. Moreover, in anionic polymerization, stringent polymerization conditions are required (Kaneko *et al*., 2006).

Therefore, functionalization or grafting a polar group onto the sPS backbone seems to be a desirable way to solve the problem of having poor impact and tear resistance and a low surface energy. So far, several attempts have been made to prepare functionalized and grafted sPS in our laboratory and other laboratories. These attempts include sulfonated sPS, maleic-anhydride grafted sPS, hydroxylated sPS and arylated sPS (Li *et al*., 2001; Zinck *et al*., 2009; Lim *et al*., 2002; Li *et al*., 2002; Liu and Sen, 2000; Gao *et al*., 2005). The present work is designed to synthesize graft (sPS-g-PS) and block [sPS-g-(PS-b-PMS)] copolymers onto sPS by utilizing the NMRP of styrene and p-methylstyrene monomers by TEMPO initiator from nitroxide mediated sPS macroinitiator and the ATRP of methacrylate monomers after bromination of the obtained graft copolymer. The α-ph-ch-sPS macroinitiator was prepared from the acid-catalyzed halogenation reaction of sPS, which was synthesized in a heterogeneous process with a-phenyl chloroacetyl chloride and anhydrous aluminum chloride in carbon disulfide via a Friedel–Crafts acylation reaction.

EXPERIMENTAL

Materials

Syndiotactic polystyrene and TEMPO were prepared by the method reported previously by our research group (Rahmani *et al*., 2007; Bani *et al*., 2004). Styrene (Tabriz Petrochemical Co., Iran), p-methylstyrene and methyl methacrylate (Merck) were distilled under reduced pressure from CaH_2 before use. Toluene and THF (Merck) were dried by refluxing over sodium and distilled under argon prior to use. N-bromosuccinimide (NBS) from Merck was purified by recrystalization in water at 70°C. 2,2′-azobis(isobutyronitrile) (AIBN) from Aldrich, were recrystallized in ethanol at 50°C. Sodium L-(+)-ascorbate was obtained from Merck and used without purification. Aluminum trichloride was purchased from Aldrich. All other reagents were purchased from Merck and purified according to the standard methods.

Instrumentation

FTIR spectra were obtained on a Shimadzu 8101M FT-IR. The samples were prepared by grinding the dry powders with KBr and compressing the mixture to form disks. The disks were stored in a desicator to avoid moisture absorption. Spectra were recorded at room temperature. ^{1}H NMR spectra were obtained at 25°C on a Brucker FT-NMR (400 MHz) spectrometer. Sample for ^{1}H NMR spectroscopy was prepared by dissolving about 10 mg of product in 5 ml of deuterated chloroform. DSC analyses were carried out using a NETZSCH (Germany) - DSC 200 F3 Maia. The sample was first heated to 200°C and kept for 5 min to eliminate the heat history. The sample was then cooled down at a rate of 10°C/min. Then the sample was reheated to 200°C at a rate of 10°C/min. The entire test was performed under nitrogen purging at a flow rate of 50 ml min^{-1}.

Synthesis of Acetylated Syndiotactic Polystyrene

Friedel–Crafts acylation was performed in a heterogeneous process, according to Scheme 1. Thus, 0.6 g of sPS, prepared previously, was suspended in 40 mL of CS_2 in a two-necked, round-bottom flask fitted with a condenser and a $CaCl_2$ guard tube. The reaction system was maintained at a temperature of 20°C and stirred vigorously with a magnetic pellet.

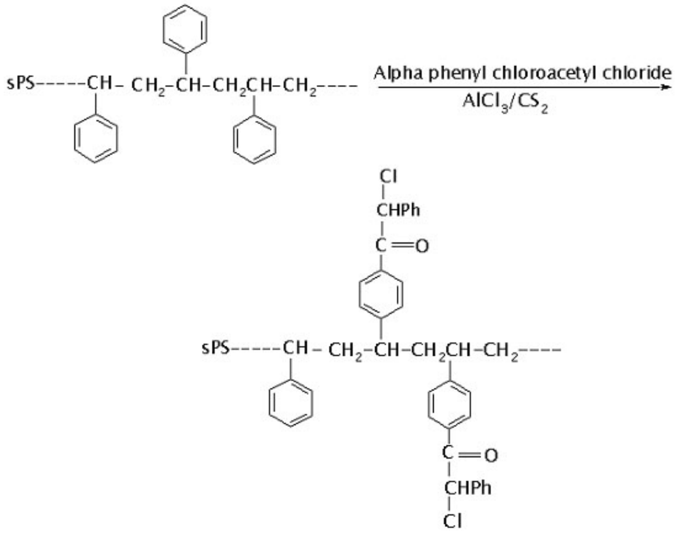
Then 2.0 g of $AlCl_3$ (0.015 mol) was added rapidly. After the mixture turned orange-red, 2.2 ml (0.015 mol) of α-phenyl chloroacetyl chloride was added through a dropping funnel after dilution with 20 mL CS_2. The reaction was conducted at a temperature of 20°C for 3 hours and then terminated by the addition of ice water followed by concentrated hydrochloric acid. The polymer was filtered, washed several times with distilled water, and dried under vacuum at temperature 70°C.

Yield: 1.05 g (white powder) (30 %).

FTIR (KBr, cm^{-1}OK): 3053 (phenyl protons of α-phenyl-chloroacetyl chloride and sPS), 2951 (aliphatic protons of a-phenyl-chloroacetyl chloride and sPS), 1729 (-CO- group of α-phenyl-chloroacetyl chloride), 1311 (-PhCHCl- groups of α-phenylchloroacetyl chloride).

Preparation of sPS -TEMPO

In a two-neck round-bottom flask equipped with condenser, dropping funnel, gas inlet/outlet, and a magnetic stirrer, 0.051 g (0.33 mmol) of TEMPO-OH that was synthesized by our research group previously (Shoaeifar *et al.*, 2007) was dissolved in anhydrous N,N-dimethylformamide (DMF) (1 ml) and added under N_2 atmosphere to 8.0 mg (0.33 mmol) of hexane-washed NaH (from 60% suspension in oil). The mixture was stirred for 30 minutes, and then 1 g of α-Phenyl-chloroacetylation of sPS was added under N_2 and refluxed for 24 hours. The reaction was terminated by pouring the content of the flask into a large amount of acidic methanol. The white solid was filtered and dried in vacuum (1.1 g) (70%).



Scheme 1: Friedel–Crafts acylation of syndiotactic polystyrene

Living Radical Graft and Block Polymerization of Styrene and p-Methylstyrene Onto Syndiotactic Polystyrene

0.4 g of the macroinitiator (sPS-TEMPO) and 5 ml (0.043 mmol) of styrene or p-methyl styrene were placed in an ampoule (20 cm in diameter), degassed with several freeze-pump-thaw cycles, sealed off under vacuum and placed in an oil bath. The solution was stirred by using an orbital shaker and heated at 125°C. During the reaction, the viscosity of the solution was observed to gradually increase. After 14 hours, the solution was dissolved in 10 mL of CH_2Cl_2 and precipitated in 50 ml of hexane for 24 hours and reprecipitated from CH_2Cl_2 into 50 mL of methanol. The crude product was dried in vacuum and weighed (yield: 80%). The crude product was extracted with cyclohexane at 30°C three times in order to remove ungrafted atactic polystyrene. Residual atactic homopolystyrene could not be observed. The purified product was dried in vacuum and weighed (Scheme 2). Yield: 0.79 g (16%)

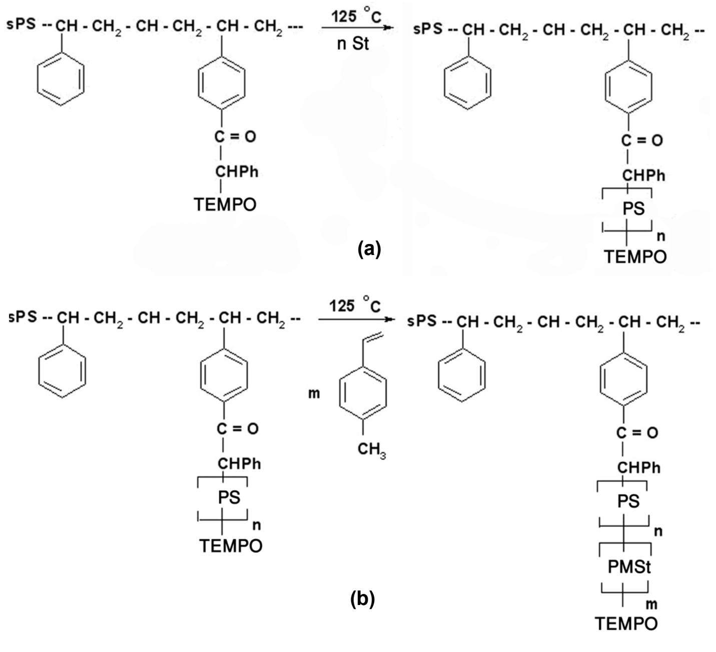
Bromination of sPS-g-(PS-b-PMS)

N-bromosuccinimide (NBS, 0.2 g) and AIBN (0.03 g) were added to a suspension of syndiotactic sPS-g-(PS-b-PMS) (1 g) in CCl_4 (40 mL) in a 100 mL round bottomed flask with a magnetic stirring bar. After refluxing at 70°C for 5 h, the reaction mixture was filtered, washed well with acetone and then dried overnight under vacuum for 24 h. Yield: 1.09 g.

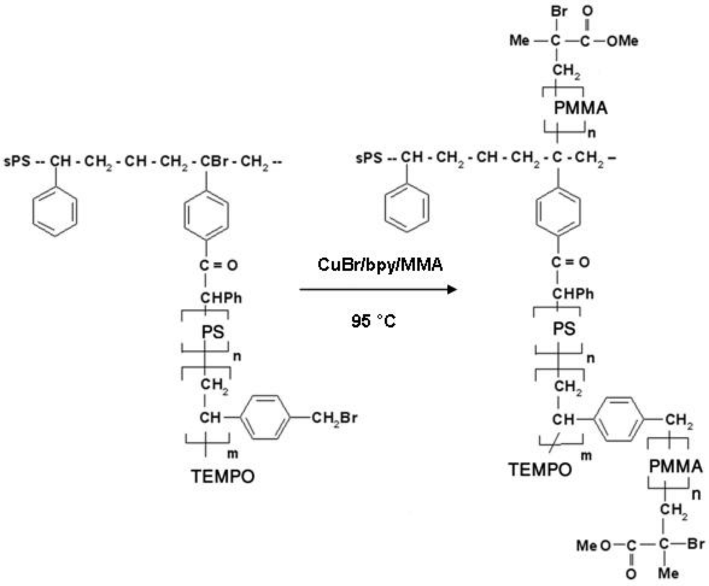
Preparation of [sPS-g- (PS-b-PMS)]-g-PMMA

In a typical experiment, a dry round-bottomed flask fitted with a 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 brominated sPS-g-(PS-b-PMS) (0.2 g). The flask was sealed and three cycles of freeze-pump-thaw were performed to remove oxygen. Then the flask was filled with purified nitrogen and the reaction mixture was heated at 90°C for 10 h with stirring. The reaction was terminated by pouring the contents of the flask into a large amount of acidic methanol. The precipitated polymer was filtered, washed several times, and dried under vacuum (Scheme 3).

The powder obtained was extracted with cyclohexane at 30°C three times to remove poly(methyl methacrylate) homopolymers. We observed no homopolymers in this condition.



Scheme 2: Living radical graft and block polymerization of styrene (a) and p-methylstyrene onto syndiotactic polystyrene (b)



Scheme 3: Preparation of [sPS-g- (PS-b-PMS)]-g-PMMA

RESULTS AND DISCUSSION

In our previous work, we reported an efficient procedure for the preparation of acetylated sPS in a heterogeneous process through the Friedel–Crafts acetylation reaction and an efficient procedure for the synthesis of controlled graft onto sPS by the atom transfer radical polymerization (ATRP) method (Abbasian *et al*., 2007). Powdered sPS was partially acetylated using α-phenyl chloroacetyl chloride as the acetylating agent and anhydrous aluminum chloride as the catalyst in carbon disulfide. The final product of chloroacetylation reaction is an aromatic ketone. Following this procedure, controlled graft and block copolymers were synthesized by ATRP and NMRP techniques.

Synthesis of Graft Copolymer Onto Syndiotactic Polystyrene

In order to produce the active sites on syndiotactic polystyrene, TEMPO was added to sPS. After the alpha chloro acetylation of syndiotactic polystyrene, OH-TEMPO reacts with α-ph-ch-sPS to give the macroinitiator sPS-TEMPO. In accord to our previous work (Abbasian *et al*., 2007), it was observed that no cross-linking reaction took place under this condition, because we added TEMPO-OH under mild and controlled condition. The anion of TEMPO was prepared and then chloroarylated sPS was added to the medium under controlled conditions. Comparison of the ^{1}H-NMR spectrum of α-ph-ch-sPS with the ^{1}H-NMR spectrum of sPS-TEMPO indicates that, during the reaction, because the chemical shift of CH–O and CH–Cl are similar, there are no changes in the chemical shifts due to the formation of CH–O, whereas the functional group of TEMPO appears with characteristic signals at 0.5–1.58 ppm (Figure 1).

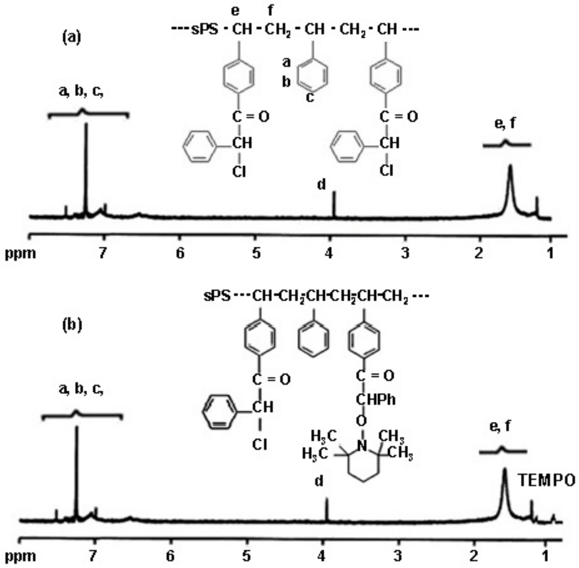


Figure 1: ^{1}H NMR spectrum of α-ph-ch-sPS (a) and the macroinitiator sPS-TEMPO (b)

The FTIR spectrum of the macroinitiator sPS-TEMPO demonstrates an absorption band at 1480 cm^{-1} which is attributed to the methyl band of TEMPO. The "C-N" and "N-O" stretching bands of TEMPO are not resolved in FTIR spectrum of the macroinitiator because these peaks overlap with the peaks of sPS (Figure 2 (a)).

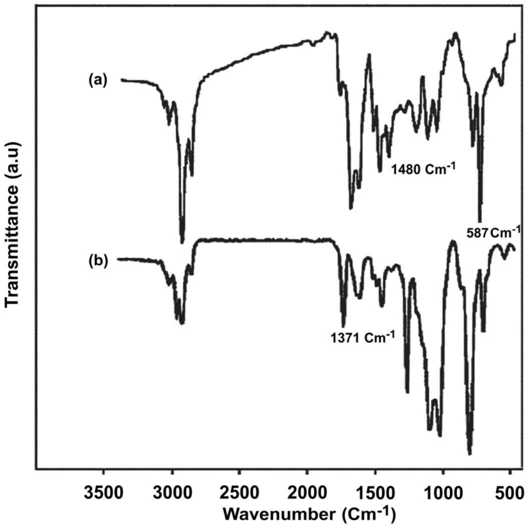


Figure 2: FTIR spectrum of the macroinitiator sPS-TEMPO (a) and the FTIR spectrum of [**s**PS-g- (PS-b-PMS)]-g-PMMA (b)

The thermal hemolytic scission of the C–O bond of the aminoxy moiety of sPS-TEMPO takes place at 125°C and causes the radical polymerization of styrene and p-methylstyrene to yield the graft (sPS-g-PS) and block [sPS-g-(PS-b-PMS)] copolymers. The bond dissociation is considered to be reversible. The crude polymerization product was purified as described in the experimental section.

To successfully carry out this polymerization, it was necessary to show that at this reaction temperature no spontaneous thermal polymerization occurred and that, in this reaction condition, the polymerization is living. For comparison, a blank experiment was done in the absence of TEMPO on Syndiotactic polystyrene. In this condition, no homo polystyrene or poly(p-methyl styrene) were formed in the absence of the macroinitiator under identical NMRP conditions. This suggests that the formation of homopolymer in the grafting reaction can be excluded and that the polymerization is living. ^{1}H NMR spectra of the purified products (Figure 3) indicate the formation of graft and block copolymers, since the chemical shifts at 6.39–7.25 ppm represent the aromatic protons in polystyrene and those at 1.2–2.1 ppm represent the aliphatic protons in polystyrene. Since the ratio of aliphatic hydrogens to aromatic hydrogens is 3 to 5, there is an increase in the integration intensity of the aromatic hydrogens in the ^{1}H NMR spectrum.

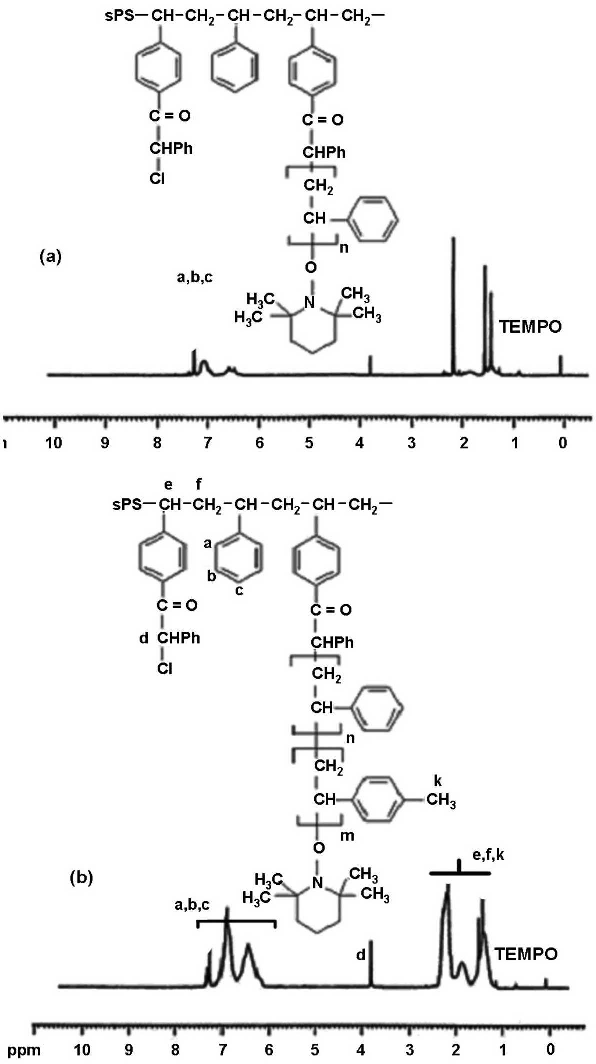


Figure 3: ^{1}H NMR spectra of sPS-g-PS (a); sPS-g-(PS-b-PMS) (b)

Bromination of sPS-g-(PS-b-PMS)

We used sPS-g-(PS-b-PMS) as the starting polymer and N-boromosuccinimide as the brominating agent to obtain polymers with a bromine group. N-Boromosuccinimide is usually used for the introduction of bromine into allylic or benzylic positions (Pizey, 1974). Thus, both the methyl groups and backbone methane carbons can be brominated in sPS-g-(PS-b-PMS). The ^{1}H NMR spectrum of brominated sPS-g-(PS-b-PMS) confirms the bromination of methyl and methine groups since the chemical shifts at 4.65 – 4.79 ppm represent the -CHBr protons in the brominated polymer. There are no changes in the chemical shift of -CHPhCl (which is related to α-ph-ch-sPS not coupled with TEMPO), whereas the integration intensity of the aliphatic hydrogens decreases. The ^{1}H NMR spectra showed that the functional groups of TEMPO were retained at the end of the polymer chains, providing strong evidence for the NMRP reaction occurring (Figure 4 (a)).

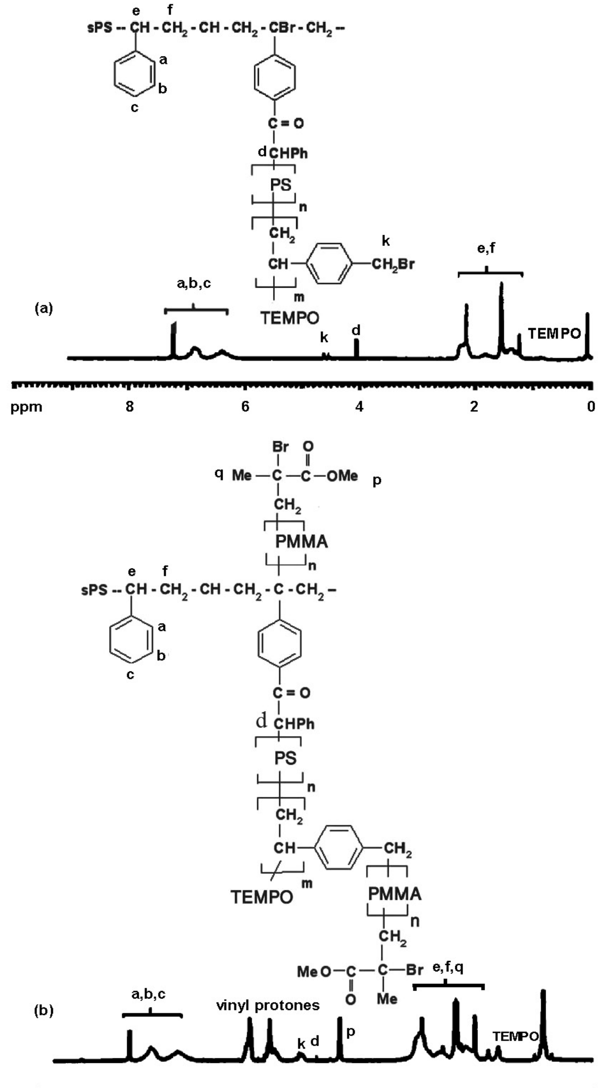


Figure 4: ^{1}H NMR spectra of sPS-g-(PS-b-PMS)-Br (a) and ^{1}H NMR Spectra of [**s**PS-g- (PS-b-PMS)]-g-PMMA (b)

Preparation of [sPS-g- (PS-b-PMS)]-g-PMMA

The synthesis of graft copolymers can be accomplished through one of the three following routes: (I) "grafting from" reactions (utilizing polymerization of grafts from a macroinitiator with pendant functionality), (II) "grafting through" processes (by homo - or copolymerization of a macromonomer) and (III) "grafting onto" (occurring when the growing chain is attached to a polymer backbone). The first two methods have been used in conjunction with ATRP in the design of graft copolymers and underscore the versatility of this controlled radical polymerization technique to synthesize a variety of copolymers. The graft copolymerization of methyl methacrylate initiated by sPS-g-(PS-b-PMS)-Br as macroinitiator in the presence of the CuBr/bpy catalyst system was first studied in anisole solvent to solubilize the catalyst and also brominated sPS-g-(PS-b-PMS) at 90°C.

The FTIR and ^{1}H NMR spectrum of the purified product (Figure 2(b) and Figure 4(b)) indicates the formation of graft copolymer [sPS-g- (PS-b-PMS)]-g-PMMA**.** In the FTIR, 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 2 (b)).

It is obvious that the peak at 587 cm^{-1} could be attributed to –CBrMe at the end of PMMA and indicates that the polymerization is living (Janata *et al*., 2001).

The ^{1}H NMR spectra of [**s**PS-g- (PS-b-PMS)]-g-PMMA is illustrated in Figure 4(b). The ^{1}H NMR spectrum of [**s**PS-g- (PS-b-PMS)]-g-PMMA displays a characteristic peak at δ = 3.61 ppm, which is related to the -OCH_3 groups of the PMMA segments, and a peak at δ = 0.8–1.1 ppm, which is related to the -CH_3 groups of the PMMA and a peak at δ = 4.65–5.15 ppm, which is related to the vinyl protons that form at the end of chain polymers.

Thermal Properties Analysis

In this work, DSC was employed to investigate the thermal properties of pure sPS and modified sPS. The DSC curves of pure sPS and grafted onto syndiotactic polystyrene are shown in Figure 5. For pure sPS, T_m and T_c are around 270 and 240°C, respectively, similar to the values previously obtained (Matyjaszewski and Xia, 2001; Srinate *et al*., 2009; Malanga, 2000). In the case of acetylated syndiotactic polystyrene, no peaks were seen, which indicated that the acetylated syndiotactic polystyrene was unable to crystallize due to the large size of the substituent group. Therefore, it is reasonable to assume that the acetylated syndiotactic polystyrene unit exists only in the amorphous region. The non-crystallizable acetylated units can interrupt or terminate crystal growth along the polymer chain (Gao and Li, 2004). Interestingly, the glass transition temperature (T_g) of syndiotactic polystyrene was found to be 98.4°C. A similar phenomenon was observed with branched oligoethene grafted sPS, as reported by Liu and Sen (2001). For the sPS-g-(PS-b-PMS) and [**s**PS-g- (PS-b-PMS)]-g-PMMA copolymers, as expected, no T_m and T_c are detected, regardless of the degree of graft, which indicates that these samples are unable to crystallize. This result is quite in agreement with that for the sPS-graft-aPS copolymers prepared by combining the metallocene polymerization technique with the marcomonomer method, as reported by Senoo *et al*. (2001). It was found that the grafted copolymers with lower content of aPS side chains could crystallize from the melt, while that with higher content of aPS was in an amorphous state. The effect of the graft chains on the crystallinity was discussed in terms of the friction force for reptation and the cohesive power. On the other hand, the T_g values of our graft copolymers differ slightly in comparison to the neat polymer. For example, the T_g of pure sPS is 99.4°C, while T_g of sPS-g-(PS-b-PMS) and [**s**PS-g- (PS-b-PMS)]-g-PMMA were found to be 99.2°C and 100.7°C, respectively.

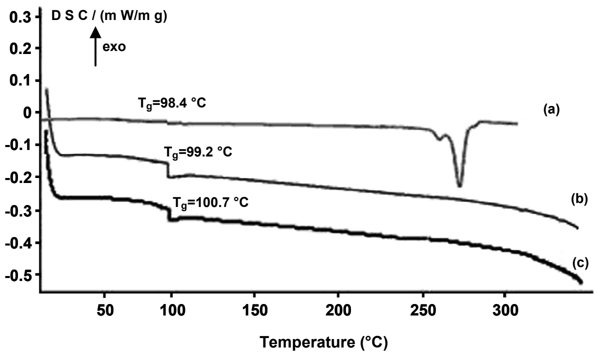


Figure 5: DSC traces of neat sPS (a), sPS-g-(PS-b-PMS) (b) and [**s**PS-g- (PS-b-PMS)]-g-PMMA (c)

CONCLUSION

We have described the efficient synthesis of a sPS graft copolymer, [**s**PS-g- (PS-b-PMS)]-g-PMMA, by the ATRP and NMRP technique. Syndiotactic polystyrene (sPS) was functionalized in the side phenyl rings with α-phenyl chloroacetyl (α-ph-ch) groups using the Friedel–Crafts reaction; the chloro groups were then converted to nitroxide mediated groups by coupling with 1-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO-OH). The resulting macro-initiator (sPS-TEMPO) for 'living' free radical polymerization was then heated in the presence of styrene and p-methylstyrene to form graft and block copolymers**.** We used sPS-g-(PS-b-PMS) as the starting polymer and N-bromosuccinimide as the brominating agent to obtain copolymers with a bromine group. This macroinitiator can polymerize methylmethacrylate monomers in the presence of the CuBr/bpy catalyst system at 90°C. 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 the catalyst, the simple polymerization procedure, and the good control of graft structure. These structures were determined by ^{1}H NMR, DSC and FT IR spectroscopy.

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NOMENCLATURE

ATRP	Atom transfer radical polymerization
NMRP	Nitroxide mediated radical polymerization
PS	Polystyrene
sPS	Syndiotactic Polystyrene
aPS e	Atactic Polystyren
PMS	Poly(p-methylstyrene)
PMMA	Poly(methyl methacrylate)
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
DSC	Differential scanning calorimetry
TEMPO-OH	4-hydroxy TEMPO
α-ph-ch-sPS	Alpha phenyl chloroacetylated syndiotactic polystyrene
LFRP	Living free radical polymerization

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