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Preparation and characterization of maleic anhydride-functionalized syndiotactic polystyrene

Hua-Ming Li[a,*], Hong-biao Chen[a], Zhi-Gang Shen[b], Shangan Lin[b]

[a]*Institute of Polymer Science, College of Chemistry, Xiangtan University, Xiangtan 411105, Hunan Province, People's Republic of China*
[b]*Institute of Polymer Science, Zhongshan University, Guangzhou 510275, People's Republic of China*

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Abstract

The free radical-induced grafting of maleic anhydride (MA) onto syndiotactic polystyrene (sPS) has been accomplished in the solution process by using 1,1,2-trichloroethane as solvent and dicumyl peroxide as free radical initiator. The amount of MA grafted on sPS was evaluated by a titration method. Grafted products separated from the reaction mixture were purified and analyzed. Fourier transform infrared spectroscopy and ^{1}H NMR studies indicate that MA attaches to the sPS in the form of single succinic anhydride rings as well as short oligomers. The results obtained by GPC analysis suggest that the degradation and chain extension reaction do not occur under the reaction conditions. Moreover, the crystallization behavior of MA-functionalized sPS was also studied by means of differential scanning calorimetry. It was found that the crystallization behavior of the grafted polymer exhibited somewhat differences in comparison to the neat sPS. The MA-functionalized sPS crystallizes at higher rate than the unmodified polymer, on the other hand, the degree of crystallinity (X_c) are lowered by the presence of the MA grafts. © 2002 Elsevier Science Ltd All rights reserved.

Keywords: Maleic anhydride; Free radical grafting; Syndiotactic polystyrene

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1. Introduction

The free radical-induced grafting of maleic anhydride (MA) onto polyolefin has been investigated extensively with a history of more than 20 years [1–6]. This large interest originates in the enhanced adhesion of MA-functionalized polyolefins to polar materials like polyamide, metals, and glass fibers. The MA-grafted polyolefins are often used as compatibilizers in polymer blends, for instance, the improvement of compatibility and mechanical properties is achieved upon blending of polyamide-6 (PA6) with various maleated polyolefins, this phenomenon is attributed to the formation of the polyamide-polyolefin graft copolymer through chemical reaction between the MA of maleated polyolefin and the amine end-group of PA6 during melt blending [5]. The functionalization of polyolefins with MA can be achieved either in a melt process [7,8] or in a solution process [9,10]. The melt state process is often called 'reactive extrusion method', where the molten polymer is mixed with MA and an initiator in an extruder at elevated temperature achieved. While in a solution process, the polymer is dissolved in a suitable solvent at elevated temperatures, and MA is added together with initiator.

At present, the based polyolefins, such as polyethylene (PE), polypropylene (PP), ethylene–propylene copolymers (EPMs) [1,2], atactic polystyrene (aPS) [3] and styrene-*b*-(ethylene-*co*-1-butene)-*b*-styrene triblock copolymer (SEBS) [4], functionalized with MA have been greatly studied and the reaction scheme of which has been well known. De Groot et al. [1] studied the structure of MA-grafted polyolefins using [2,3-$^{13}C_2$] MA by means of ^{13}C NMR spectroscopy. It was found that MA attached to PE in the form of single succinic anhydride rings as well as short oligomers, in (co)polymer with abundant tertiary hydrogen atoms, such as alt-EPM and PP, MA chiefly in the form of single succinic anhydride rings. However, up to the present no studies on MA-functionalized syndiotactic polystyrene (sPS) were reported.

sPS is a new semicrystalline polymer, which has attracted much interest due to several desirable physical properties. The most intriguing properties of sPS are high melt temperature, high crystallinity and rapid crystallization rate. Therefore, sPS exhibits not only good chemical resistance but enhanced mechanical performance at elevated

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* Corresponding author. Tel.: +86-732-829-2567; fax: +86-732-829-2373.

E-mail address: lhm28@21cn.com (H.M. Li), huamingli8@163.com (H.M. Li).

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temperatures as well [11–15]. However, a certain disadvantage of sPS is its inherent brittleness [16]. Thus, an application of sPS might be found predominantly in blends or compositions. The practice of blending sPS with engineering thermoplastics (e.g. polyamides), just as in the toughening of isotactic polypropylene (iPP) [17–19] seems to be the best way out. It is well known that immiscible polymer blends often exhibit poor mechanical properties due to poor physical and chemical interactions across the phase boundaries [20]. A way to overcome this problem is through the use of compatibilizers, which are capable of acting as an emulsifier and reducing the interfacial tension in polymer blends [20]. The usually used compatibilizers are block or graft copolymers. However, block copolymers have disadvantages such as difficulty in their synthesis. In this respect, MA grafted polymers may be better suited for using as compatibilizer in polymer blends.

In this paper, we focused our investigation on the preparation of MA-functionalized sPS in a solution process. As mentioned before, sPS crystallizes very rapidly and exhibits a high melting point of about 270 °C. Therefore, functionalization reaction in a melt state is very difficult. On the other hand, the rapid crystallization adds a formidable barrier to dissolving the polymer. Thus, the solubility and gelation characteristics of sPS must bee considered in developing a homogeneous, solution state, functionalization procedure.

2. Experimental

2.1. Materials

The sPS used in these studies was synthesized by bulk polymerization of styrene with a $Cp^*Ti(OCH_2C_6H_5)_3/MAO$ catalytic system at 80 °C [15]. The resulting polymer was stirred in a 5 wt% methanol solution of HCl for 2 h to remove the residual metal catalyst, the polymer was then filtered and dried under vacuum at 70 °C for three days after which was extracted with methylethylketone (MEK) overnight to remove the atactic component. The unextracted fraction was characterized to have a very high steric purity (>99% in syndio units, calculated via ^{13}C NMR spectroscopy) and its number-average molecular weight and polydispersity were 210,000 and 2.2, respectively, as determined by gel-permeation chromatography (GPC) using 1,2,4-trichlorobenzene as a solvent at 130 °C, against standard polystyrene.

MA was recrystallized from benzene and sublimed in vacuum before use, the melting point of purified MA is 52.7 °C. Dicumyl peroxide (DCP, Aldrich) was used without further purification. 1,1,2-trichloroethane (TCE) and chloroform were dried overnight with anhydrous calcium chloride and then distilled before use.

2.2. Functionalization reaction

Functionalization of sPS was performed in the solution-grafting experiments. In a typical solution-grafting process, 5 g of sPS was dissolved in 250 ml TCE at 115 °C under a nitrogen atmosphere. After complete dissolution of the sPS, 2.5 g of MA was added, the radical initiator DCP (600 mg) was added to the hot liquid mass in three increments (200 mg, each) at regular intervals of 16 h. The reaction was allowed to proceed for 48 h at ca. 110 °C under stirring and then cooled to about 80 °C. Note that at 80 °C, solution state crystallization and subsequent gelation occurred for sPS solution concentrations in TCE greater than ca. 3% (w/v). To avoid gelation (i.e. solution crystallization), the warm solution (about 80 °C) was poured out into 2000 ml of acetone to precipitate the grafted polymer. The product was washed thoroughly with boiling acetone for five times and subsequently dried in vacuum at 80 °C for 72 h.

2.3. Determination of MA content

The amount of MA grafted on sPS was determined from the anhydride concentration presented in the functionalized polymer. After dissolution of 1 g of sample in 200 ml of chloroform at boiling temperature, about 5 μl of water was added to hydrolyze anhydride functions into carboxylic acid functions. The boiling temperature was maintained for 10 h. Then the solution was titrated to a phenolphthalein end point using potassium hydroxide in methanol. The functionalized sPS (sPS-*g*-MA) was completely soluble at the boiling temperature of chloroform and did not precipitate during the titration. The acid concentration was easily converted to the MA content as follows:

$$\mathrm{MA(wt\%)} = [(98 \times N \times V)/(2 \times W)] \times 100\%$$

Where N and V are the concentrations (mol/l) and volume (l) of potassium hydroxide–methanol standard solution, respectively. W (g) is the weight of the MA-functionalized sPS sample.

2.4. Size exclusion chromatography (SEC) analysis

The molecular weight of the MA-functionalized polymers was determined by SEC calibrated with polystyrene standards using Waters 150C equipped with three Shodex columns (two of Shodex AT-80M/S and one of Shodex Styragel 300A) with 1,2-dichlorobenzene (stabilized with 1% Irganox 1010) as an eluent at 130 °C.

2.5. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were recorded on a Perkin–Elmer Spectrum One spectrometer from 4000 to 400 cm^{-1} with a 2 cm^{-1} resolution. Thin films, 25–60 μm thickness, were prepared by compression-molding at 285 °C under 5 MPa for 1 min.

Table 1
Feed composition and GPC analysis of the products in functionalization reaction of sPS

Run	DCP (g)	Reaction time (h)	MA content (wt%)	M_n ($\times 10^3$) (g mol^{-1})	M_w ($\times 10^3$) (g mol^{-1})	M_w/M_n
FsPS0[a]	0.6	48		221	464	2.1
FsPS1	0.6	3	0.1	221	465	2.1
FsPS2	0.6	9	0.19	222	466	2.1
FsPS3	0.6	18	0.45	221	486	2.2
FsPS4	0.6	30	0.81	224	470	2.1
FsPS5	0.6	48	1.16	226	497	2.2
FsPS6	0.1	30	0.11			
FsPS7	0.2	30	0.23			
FsPS8	0.3	30	0.36			
FsPS9	0.4	30	0.57			
FsPS10	0.5	30	0.72			

All experiments are carried out at 110 °C under a nitrogen atmosphere using 1,1,2-trichlorothane (TCE, 250 ml) as solvent with a fixed sPS/MA mass ratio of 2:1, (sPS = 5.0 g, MA = 2.5 g).

[a] FsPS0 is the blank experiment which processed in the presence of DCP but without MA.

2.6. ^{1}H NMR spectroscopy

NMR spectra were recorded with a INOVA 500 spectrometer. Samples for ^{1}H NMR spectroscopy were prepared by dissolving about 100 mg of products in ~5 ml of deuterated chloroform. Tetramethylsilane were used as an internal standard.

2.7. Thermal analysis

Thermal analysis was performed using a TA instruments DSC-2910 under nitrogen atmosphere. For all samples, the following procedure was used: samples were heated at 295 °C for 5 min in order to eliminate the influence of thermal history and the effect of heat treatment on the crystalline structure of the materials, then cooled down to 30 °C to record the crystallization temperature, and then reheated to 295 °C, all at a rate of 20 °C/min. The recorded temperatures were calibrated using Indium as standard.

3. Results and discussion

3.1. Preparation and MA content of modified sPS

As mentioned previously, polyolefins functionalized with MA by a radical process have been greatly studied. These polyolefins include PE, PP, EPMs and SEBS [1–3]. But for aPS, the literature contains conflicting points on the grafting of MA onto aPS by a radical process. Xue et al. [21] considered that the initiator is unable to remove a hydrogen atom from aPS, and therefore there is no evidence to suggest that graft copolymerization onto aPS may be accomplished by a radical process. On the other hand, Jo [3] and Passaglia [4] invoked an argument based on experimental results that grafting of MA onto aPS can be accomplished through a radical process, although the reaction mechanism is not clarity.

In this paper, we try to functionalize sPS with MA in a solution process. However, functionalization reaction in a melt state was proved to be very difficult, since sPS is a semicrystalline polymer and with a high melting point of about 270 °C. In the solution-grafting experiments, TCE and DCP were used as solution and free radical initiator, respectively. The polymer after the functionalization reaction was treated with boiling acetone to remove unreacted monomer, DCP residues and MA oligomer, if present. It is of great importance to insure total elimination of all the unreacted MA and homopolymer of MA. Since unreacted monomer and MA oligomer may prevent accurate characterization of the modified polymer and accurate determination of the grafted anhydride concentration.

Table 1 lists the results of the sPS functionalization reactions. All experiments carried out with a variable amount of DCP (variable MA/DCP mass ratio) and using a fixed sPS/MA mass ratio of 2:1. The MA contents of the modified sPS depended upon both the amount of DCP and the reaction time, and increased with increasing the amount of DCP as well as the reaction time. It is worth noting the unusual long reaction time and high MA concentration that are needed in the sPS functionalization reactions with respect to other polyolefins, such as PP, PE and EPMs, functionalization reactions [1]. This phenomenon indicated that the grafting reactions proceeded very slowly.

Molecular weights of grafted products are also summarized in Table 1. The values of molecular weight and molecular weight distribution (M_w/M_n) of functionalized sPS are nearly the same as those of neat sPS. This suggests that significant crosslinking and chain scission of sPS can be excluded in this study. This result is in agreement with the result of the MA-grafted aPS prepared from the radically initiated grafting reaction in melt state as reported by Jo [3]. Degrees of grafting obtained here are lower than 1.2 wt%.

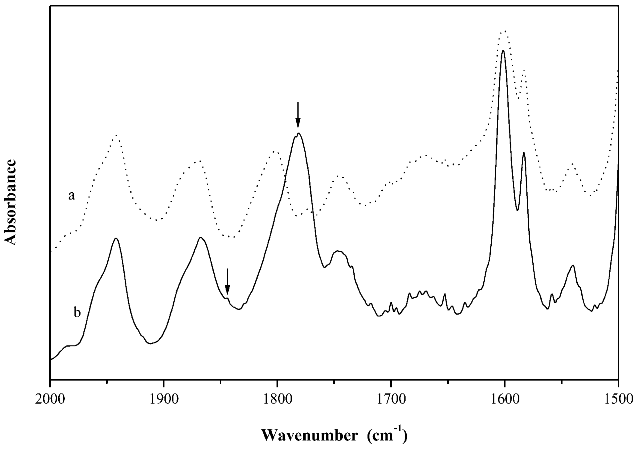

Fig. 1. FTIR spectra of (a) sPS (FsPS0) and (b) MA-functionalized sPS (FsPS5) with MA content of 1.16 wt% compression molded films.

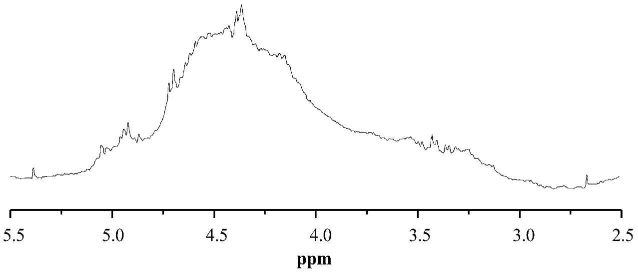

Fig. 2. ^{1}H NMR spectrum of poly(MA) separated from acetone soluble fraction in Run FsPS5.

3.2. Characterization of functionalized sPS

The grafted polymer was confirmed using both FTIR and NMR spectroscopy. Fig. 1 shows the FTIR spectra of FsPS0 and FsPS5 (see Table 1) in the range 2000–1500 cm^{-1}. FsPS0 is the product of sPS processed in the presence of DCP but without MA (blank experiment). Sample FsPS5 is the MA-functionalized polymer with a MA content of 1.16 wt%. Before testing, it was dried at 120 °C for 24 h under vacuum in order to transform carboxylic acid into carboxylic anhydride which could be confused with FTIR spectra analysis.

In the spectrum of FsPS5 (Fig. 1(b)), a broad and intense absorption band at about 1780–1784 cm^{-1} and a weak absorption band at 1843 cm^{-1}, not observed in the spectrum of FsPS0, are found. The new absorption bands at 1780–1784 cm^{-1} and at 1843 cm^{-1} can be assigned to grafted anhydride, which are due to symmetric (strong) and asymmetric (weak) C=O stretching vibration of five members cyclic anhydrides [22,23], respectively. It is important to note the much broad new absorption bands at about 1780–1784 cm^{-1} as shown in Fig. 1(b), which indicates that MA may be attached to the sPS in the form of short oligomers as well as single succinic anhydride rings based on the identification of the MA-grafted PP as reported by De Roover et al. [2]. They found that PP-*g*-MA prepared in a melt process contains single or even polymeric grafts, exclusively attached to the chain ends of PP as evident by the appearance of the new overlapping absorption bands at 1792 and 1784 cm^{-1} in the FTIR spectrum. The absorption band at 1784 cm^{-1} is attributed to poly(maleic anhydride) (poly(MA)) grafts while the band at 1792 cm^{-1} to succinic anhydride end-groups. Furthermore, when poly(MA) and citraconic anhydride were selected as model compounds and blended in molten PP, the anhydride showed a characteristic absorption band at 1784 and 1780 cm^{-1}, respectively, [2]. Therefore, it can be thought that the broad absorption bands at 1780–1784 cm^{-1} observed in MA-functionalized sPS correspond to anhydrides of MA oligomers and single anhydride rings. The difference in the position of anhydride absorption bands between PP-*g*-MA and MA-functionalized sPS may be due to the difference of the based polymers.

From the results of Infrared analysis, it can be deduced that grafting of the single anhydride rings as well as oligomers take place during the functionalization of sPS under this reaction conditions. In order to verify this conclusion, the experiment of Run FsPS5 was repeated and the acetone-soluble fraction was collected. The acetone and TCE was removed by using a rotary vacuum evaporator at about 45 °C. The solid materials was purified by dissolving in 50 ml of boiling acetone and then precipitating in 400 ml of toluene. The precipitate was filtered, washed with toluene, and dried in vacuum at 60 °C. About 12 mg of which was obtained. ^{1}H NMR analysis demonstrated that the product was poly(MA) (Fig. 2) and its molecular weight (M_n) was about 600. This result conclusively supports the argument that oligomerization of MA and oligomeric grafts can occur under this conditions. Russell [10] studied the solution grafting reaction between MA and hydrocarbons (i.e. eicosane and squalane) at 60 and 80 °C with 1,2-dichlorobenzene as solvent. The formation of oligomeric grafts was also found and Russell attributed this to the fact that the reaction was carried out below the ceiling temperature of MA polymerization, which is estimated to be 108 °C for 1 M and 90 °C for 0.4 M monomer concentration. However, this temperature seems quite low after examination of the results presented in this article (about 110 °C) and with those dealing with the homopolymerization of MA at about 150 °C reported elsewhere [24]. Furthermore, even though the reaction temperature is much high, for instance, in the melt grafting process at about 190 °C, oligomerization of MA is also possible [2]. The fact that many experimental results do not provide support to a clear correlation between ceiling temperature and the occurrence of oligomeric grafts indicate that it may be inaccurate to use ceiling temperature to preclude the homopolymerization of MA.

Supporting evidence for the conclusion that both single succinic anhydride rings and MA oligomers are attached to the sPS chain comes from a comparison of the ^{1}H NMR spectra of poly(MA) and that of the MA-modified sPS. Fig. 2 shows the ^{1}H NMR spectrum of homopolymer of MA.

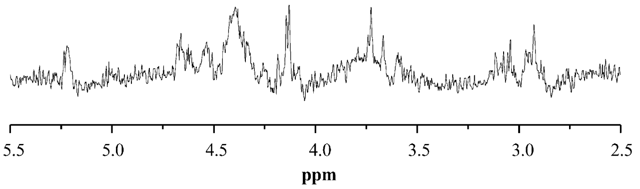

Fig. 3. ^1H NMR spectrum of MA-functionalized sPS (FsPS5) with MA content of 1.16 wt%.

There is a broad group of complex resonances centered on 4.5 ppm, which is characteristic of poly(MA) chains and is similar to the ^1H NMR spectrum of poly(MA) as reported in Ref. [25]. The broad resonance between 3 and 5.2 ppm is attributed to the CH-groups forming the backbone.

Fig. 3 shows the ^1H NMR spectra of the MA functionalized sPS (FsPS5). There are four major weak resonances in the 2.5–5.5 ppm with chemical shifts of about 2.8–3.2, 3.5–4.0, 4.0–4.8 and 5.2 ppm. By comparison of this spectrum with that of poly(MA) as shown in Fig. 2, it can be conclude that MA was attached to the sPS chains in the form of single succinic anhydride rings as well as short oligmers since neat sPS has no resonances in this region. The resonances at 2.8–3.2 and 3.5–4.0 ppm are assigned to the methane proton and the methylene protons of the succinic anhydride ring, respectively, which suggests that the grafts consist of single succinic anhydride rings [26]. On the other hand, additional resonances at 4.0–4.8 and 5.2 ppm were observed in Fig. 3, which probably arise from the sidechains containing more than one succinic anhydride unit, revealed the presence of oligomeric grafts [10]. Grafts containing single succinic anhydride rings must not absorb to a significant extent to lower field of 4 ppm [26]. Since poly(MA) gives a spectrum is confined to the 3.0–5.0 ppm, the broad group of resonances is centered on 4.5 ppm and little signal is detected below 3.5 ppm, which can be used to distinguish between polymer sidechains and single units of succinic anhydride [10]. Moreover, it is worth noting that the intensity of the resonances in 2.8–4.0 region is almost similar to that of the resonances in 4.0–5.5 region. This indicates that the proportion of oligomeric grafts (grafts containing more than one succinic anhydride unit) and grafts containing single succinic anhydride ring are nearly equal. However, the ^1H NMR spectroscopy of MA-functionalized sPS is different from that of the aPS-*g*-MA prepared in the melt process, which only showed a complex multiplet in the 3.5–3.8 region [3].

Table 2
Summary of DSC results for sPS and MA-modified sPS

Samples	T_g (°C)	T_m (°C)	ΔH_f (J/g)	X_c (%)[a]	T_c (°C)[b]	ΔH_c (J/g)[b]
SPS	95.6	262.0/270.4	31.72	59.8	238.7	31.54
FsPS3	96.4	266.2/270.6	29.61	55.9	235.6	28.76
FsPS4	95.6	264.9/270.4	26.64	50.3	235.8	27.01
FsPS5	97.2	254.1/266.4	24.20	45.7	233.5	21.32

[a] The crystallinity of the sample, X_c, is determined by the equation: $X_c = (\Delta H_f/\Delta H_f^0)\times 100$, where ΔH_f is the melting enthalpy of the sample and ΔH_f^0 is the melting enthalpy of 100% crystalline sPs ($\Delta H_f^0 = 53$ J/g [29]).

[b] The crystallization temperature (T_c) and crystallization enthalpy of the sample are determined from the DSC cooling scans from melt at 295 °C at a cooling rate of 20 °C/min.

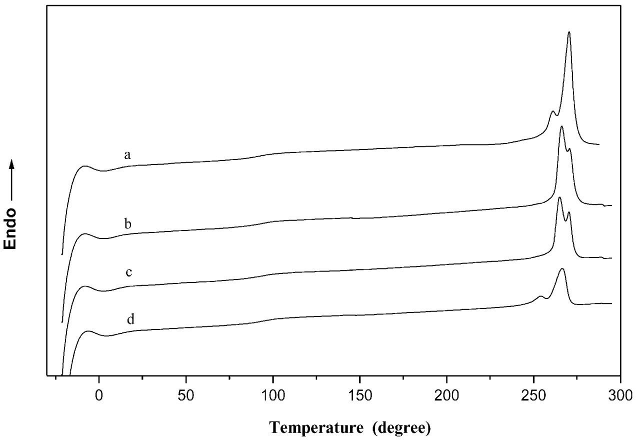

Fig. 4. DSC scans of (a) sPS and MA-functionalized sPS with different MA contents, (b) 0.45 wt%, (c) 0.81 wt% and (d) 1.16 wt%.

3.3. Thermal analysis

sPS is a semicrystalline polymer and its properties are related to its morphological features such as degree of crystallization, size (thickness and lateral dimension of lamellae) and perfection of crystallites [27]. Therefore, it is important to study the crystallization behavior of MA-functionalized sPS. Previously investigations of maleated semicrystalline polymers, such as polypropylene-based systems, have demonstrated that the degree of crystallinity decreased while the rate of crystallization increased [28].

In order to understand the link between MA grafts and crystallization in maleated sPS, we are beginning to investigate the crystallization behavior of sPS-*g*-MA copolymers by means of DSC. Fig. 4 shows DSC scans of (a) sPS and sPS-*g*-MA copolymers with different MA contents ((b), 0.45 wt%, (c), 0.81 wt% and (d), 1.16 wt%). Prior to collecting the heating scan data, the samples were first heated to 295 °C and kept at this temperature for 5 min, then cooled at a rate of 20 °C/min to the start temperature. The crystallization temperature (T_c) was recorded from the cooling scans of the samples (Fig. 5). Table 2 lists the thermal data for each of the samples shown in Figs. 4 and 5. The data in Table 2 exhibit a systematic trend of degree of crystallinity (X_c) depression with increasing MA content. The degree of crystallinity (X_c) of the sample was determined by measuring the enthalpic change at melt. For the sample with MA content of 1.16 wt% (curve (d)), its X_c value is 45.7%, lower than that of neat sPS (59.8%). However, after grafting with MA, the values of melting point (T_m) decreased little or did not change. Only when the MA content reached 1.16 wt%, its T_m is 254/266 °C, somewhat lower than that of neat sPS (262/270 °C). This indicated that the incorporation of MA grafts along the sPS

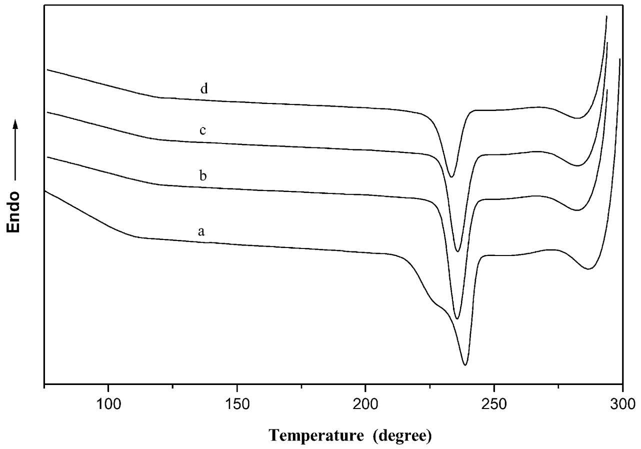

Fig. 5. DSC cooling curves of (a) sPS and MA-functionalized sPS with different MA contents, (b) 0.45 wt%, (c) 0.81 wt% and (d) 1.16 wt%.

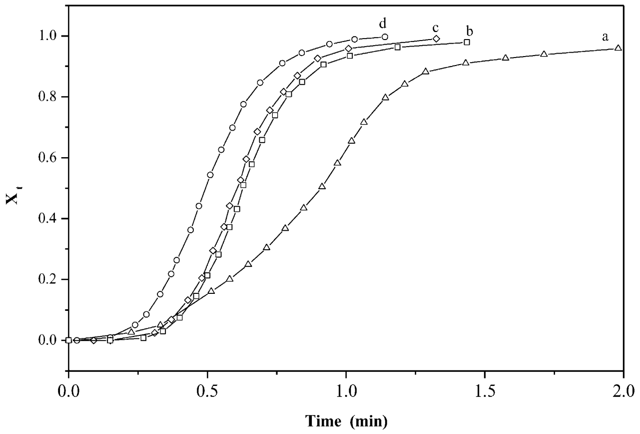

Fig. 6. Fractional crystallization versus time profiles for (a) sPS and MA-functionalized sPS with different MA contents, (b) 0.45 wt%, (c) 0.81 wt% and (d) 1.16 wt%, nonisothermally crystallized at a cooling rate of 20 °C/min.

backbone has little effect on the crystal perfection of sPS, although there are some effects on the degree of crystallization.

To better understanding the effects of MA grafts on the crystallization of sPS-*g*-MA copolymers, nonisothermal crystallization kinetics studies were performed. Fig. 6 compares the fractional crystallization, X_t, versus time profile of sPS to those of copolymers with different MA contents. These crystallization profiles were obtained at a cooling rate of 20 °C/min (Fig. 5). It is clear in Fig. 6 that the sPS-*g*-MA copolymers crystallize over a shorter period of time relative to the pure sPS sample. This is in agreement with He's finding [28].

The glass transition temperature (T_g) data also helps in understanding the effects of MA grafts on the movement of copolymer chains. It is clear from Table 2 that the T_g values of the modified polymer alter slightly in comparison to the neat polymer.

4. Conclusions

MA-functionalized syndiotactic polystyrene was prepared in a solution grafting process at 110 °C by using 1,1,2-trichloroethane as solvent and dicumyl peroxide as radical initiator. FTIR and ^{1}H NMR spectra were used to confirm that maleated syndiotactic polystyrene was the product of the functionalization reaction. MA attached to the sPS in the form of single succinic anhydride rings as well as short oligomers. The results obtained by GPC analysis indicate that the degradation and chain extension reaction do not occur under the reaction conditions. In addition, it is found that the crystallization behavior of the grafted polymer exhibited somewhat differences in comparison to the neat sPS. The MA-functionalized sPS crystallizes at higher rate than the unmodified polymer, while the values of the degree of crystallinity (X_c) were lowered by the presence of the MA grafts. In addition, the melting points (T_m) of the maleated syndiotactic polystyrene samples changed little or did not change.

Acknowledgments

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References

[1] Heinen W, Rosenmoller CH, Wenzel CB, De Groot HJM, Lugtenburg J. Macromolecules 1996;29:1151.
[2] De Roover B, Sclavons M, Carlier V, Devaux J, Legras R, Momtaz A. J Polym Sci, Polym Chem 1995;33:829.
[3] Jo WH, Park CD. Polymer 1996;37:1709.
[4] Passaglia E, Ghetti S, Picchioni F, Ruggeri G. Polymer 2000;41:4389.
[5] Hobbs SY, Bopp RC, Watkins VH. Polym Engng Sci 1983;23:380.
[6] Majumdar B, Keskkula H, Paul DR. Polymer 1994;35:1386.
[7] Watanabe W, Hatakeyama T. J Appl Polym Sci 1989;37:1141.
[8] Ho RM, Su AC, Wu CH, Chen SI. Polymer 1993;34:3264.
[9] Ruggeri G, Aglietto M, Petragnani A, Ciardelli F. Eur Polym J 1983;19:863.
[10] Russall KE. J Polym Sci, Polym Chem 1995;33:555.
[11] Ishihara N, Seimiya T, Kuramoto M, Uoi M. Macromolecules 1986;19:2464.
[12] Pellecehia C, Longo P, Grassi A, Ammendola P, Zambelli A. Makromol Chem Rapid Commun 1987;8:277.
[13] Ishihara N, Kuramoto M, Uoi M. Macromolecules 1988;21:3356.
[14] Zambelli A, Longo P, Pellecehia C, Grassi A. Macromolecules 1987;20:2035.
[15] Zhu FM, Lin S, Zhou WL, Tu JJ, Chen DQ. Chem J Chin Uni 1998;19:1844.
[16] Jones MA, Carriere CJ, Dineen MT, Baldwinski KM. J Appl Polym Sci 1997;64:673.

[17] Coran AY, Patel R. Rubber Chem Technol 1983;56:1045.

[18] Martuscelli E, Silverstre C, Abate G. Polymer 1982;23:229.

[19] Tang T, Jing X, Huang B. J Macromol Sci Phys 1994;B33:287.

[20] Noolandi J, Hong KM. Macromolecules 1984;17:153.

[21] Xue JT, Jiang D, Wilkie CA. Polym Prepr (Am Chem Soc Div Polym Chem) 1996;36(2):140.

[22] Bellamy LJ. The infrared spectra of complex molecules. New York: Wiley; 1964.

[23] Pouchert CJ. The Aldrich library of infrared spectra. Aldrich Chemical Company; 1970.

[24] Kellou MS, Jenner G. Eur Polym J 1976;12:883.

[25] Regel W. Markromol Chem 1981;182:237.

[26] Russall KE. J Polym Sci, Polym Chem 1988;26:2273.

[27] Su Z, Li X, Hsu SL. Macromolecules 1994;27:287.

[28] Jian Y, He J. Acta Polym Sinica (Chinese) 1999;(3):187.

[29] De Candia F, Filho AR, Vittoria V. Colloid Polym Sci 1991;269:650.