



## Preparation and Characterization of Maleic Anhydride Modified Syndiotactic Polystyrene

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### ABSTRACT

Maleic anhydride (MA) modified syndiotactic polystyrene (sPS) was accomplished via Friedel-Crafts acylation reaction in the presence of anhydrous aluminium chloride in a heterogeneous process. The modified polymer, maleated sPS (m-sPS), separated from the reaction mixture was purified and analyzed. FTIR spectroscopy and  $^1\text{H}$  NMR studies indicate that this chemical reaction can introduce both carboxyl groups and double bonds onto pendant aromatic groups of the polymer, which is quite different from the MA-grafted sPS prepared by a radical process, where MA attaches to the sPS aliphatic backbone in the form of single succinic anhydride rings as well as short oligomers. The results obtained by titration analysis suggest that the acylation reaction can be carried out to a higher degree of functionalization. Moreover, the thermal properties of MA-modified sPS were also studied by means of DSC. It is found that the thermal behaviour of the m-sPS exhibits considerable differences in comparison to the neat sPS. The melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), and degree of crystallinity of the maleated polymers decrease with increasing the content of carboxyl groups, while the glass transition temperature increases.

### Key Words:

syndiotactic polystyrene;  
maleic anhydride;  
Friedel-Crafts reaction;  
modification.

### INTRODUCTION

Syndiotactic polystyrene (sPS) is a new semicrystalline engineering thermoplastic [1]. With its good properties inherited from atactic polystyrene (aPS) such as low density, low dielectric constant and high modulus [2], sPS exhibits many other unique properties, superior to traditional aPS. Along

with high melting temperature (ca. 270°C), high crystallinity and rapid crystallization rate, sPS exhibits good resistance to heat and chemicals. Many performances of sPS are equal to that of other engineering plastics such as polyesters and polyamides. Therefore, sPS is prospective for a large number of

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applications in the electronic, packaging, and automotive industries. On the other hand, with high rigidity due to the phenyl ring in the polymer side chain, sPS suffers from poor impact strength, inherent brittleness, and low surface energy. Pure sPS is only used as film materials and fibres. Thus modification of sPS is necessary for extending the application fields of sPS and has been the subject of investigation.

Recently, many efforts for sPS modification have been made on the polarity improvement, toughness reinforcement through several procedures, which can be summarized as physical and chemical modification. Physical modification involves filling [3], blending [4], and composite forming [5]. Physical blending of sPS with other polymers or substrates (e.g., engineering plastics and elastomers) may extend the commercial utilities of sPS. Except for a few polymers such as aPS and poly(*p*-phenylene oxide), blending with other polymers (e.g., polyamides) usually leads to phase separation due to lack of compatibility [6]. Therefore, chemically modified sPS polymers with functional groups were expected to be desirable materials acting as compatibilizers in polymer blends since they can reduce the interfacial tension.

Dealing with the preparation of chemically modified sPS, the experimental observations were interpreted as three aspects in previous articles:

(1) Functionalized sPS can be achieved through grafting polymerization [7-9]. For example, maleated sPS has been synthesized by free radical-induced grafting reaction through either solution process [7] or solid state [8].

(2) Modified sPS can also be achieved by incorporation of other functional groups onto the polymer backbone. Examples include sulphonated sPS [10-12], brominated sPS [13] and acetylated sPS [14].

(3) The direct polymerization of styrenic monomer, or copolymerization of the monomer with a second monomer using metallocene catalyst systems to produce sPS derivatives containing functional groups. For example, Chung et al. developed a route to prepare functionalized sPS through the direct copolymerization of styrene with a borane-containing styrenic monomer and extended this sPS to prepare functionalized sPS and sPS graft copolymers [15].

In our previous report, succinic anhydride modified sPS (succinoylated sPS) has been successfully

synthesized by Friedel-Crafts reaction [16]. The outstanding virtue of this method is well suited for the preparation of high molecular mass of styrenic polymer based ionomers with substituted groups situated randomly along the polymer chain [17]. As reviewed from the literature, we found that there was limited information about the preparation of sPS bearing pendant carboxyl groups next to phenyl rings. We think that the new system of carboxylated sPS possesses the following characteristics: (i) the incorporation of carboxyl groups onto sPS can improve the polarity of the polymer, which may be used as compatibilizer for sPS based blend systems; (ii) pendant carboxyl groups, will be potentially interesting for the preparation of comb-like amphiphilic copolymers and sPS based ionomers; and (iii) carboxylated sPS can be used as model ionomers for further study.

Maleic anhydride (MA), a polar monomer, is usually used in polyolefins grafting modification [18]. MA grafted sPS, as mentioned above, has been successfully synthesized by our group [7] and Lim et al. [8] through free radical-induced grafting reaction. In our previous work, FTIR spectroscopy and <sup>1</sup>H NMR were used to characterize the graft polymer. It is found that MA attaches to the sPS in the form of single succinic anhydride rings as well as short oligomers [7]. In addition, high graft density and control over the grafted MA content were proved to be difficult to achieve by the free radical-induced grafting method. Therefore, the present study introduces another method for modifying sPS with MA via Friedel-Crafts acylation reaction in a heterogeneous condition. In the sPS Friedel-Crafts reaction, MA reacts with sPS in a way similar to succinic anhydride, but can introduce both carboxyl groups and double bonds onto pendant aromatic groups of sPS. It is important to note that the modified polymers (m-sPS) whose functional groups containing double bonds will provide a new site for further functionalization. Furthermore, a higher content of carboxyl groups can be achieved in this process (> 7 wt%) compared with the radical grafting method. The aim of this work is to modify sPS with MA via Friedel-Crafts reaction. In addition, FTIR and NMR spectroscopies were applied to characterize the modified sPS, while DSC was used to investigate the thermal properties of m-sPS in view of the crystallization and melting behaviour along

with the neat sPS.

## EXPERIMENTAL

### Materials

sPS used in these studies was synthesized by bulk polymerization of styrene with a  $Cp^*Ti(OCH_2C_6H_5)_3/MAO$  catalytic system [19] with a very high steric purity (> 99% as syndio units) and its number average molecular weight and polydispersity were 210,000 and 2.2, respectively. MA was purified by recrystallization from chloroform and dried under vacuum at room temperature before use. Carbon disulphide was dried overnight with anhydrous calcium chloride, filtered and fractionally distilled in the presence of phosphorus pentoxide before use. All the other reagents and solvents were commercially available and of analytical grade.

### Preparation of Maleated Syndiotactic Polystyrene (m-sPS)

In a typical run, 0.49 g (5.0 mmol) of MA and 2.0 g (15 mmol) of finely powdered anhydrous aluminium chloride ( $AlCl_3$ ) were treated with 50 mL of carbon disulphide in a three-necked flask equipped with condenser, dropping funnel, gas inlet/outlet, and a magnetic stirrer. After being rapidly stirred at ambient temperature for 2 h, 0.52 g (5.0 mmol based on benzene ring) of sPS (200 mesh) was added to the mixture. The reaction was continued to the corresponding time at 25°C under nitrogen atmosphere. Then, the product was decomposed with ice water followed by dilute hydrochloric acid, thoroughly washed with water to remove any residual acid, filtered and dried overnight under vacuum at 70°C. The modified polymer was refined with 1,1,2-trichloroethane/methanol mixture (99/1, v/v), then precipitated with methanol, filtered, and subsequently dried under vacuum.

### Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer spectrum. Film samples were cast in aluminium pans from a 1.0 wt% solution in chloroform/methanol mixture (99/1, v/v) and dried under vacuum at 70°C, which is sufficiently high for removal of residual solvent.

$^1H$  NMR spectra were obtained at 25°C on a Bruker AV400 NMR spectrometer. Samples for  $^1H$  NMR spectroscopy were prepared by dissolving about 10 mg of products in an appropriate amount of deuterated chloroform.

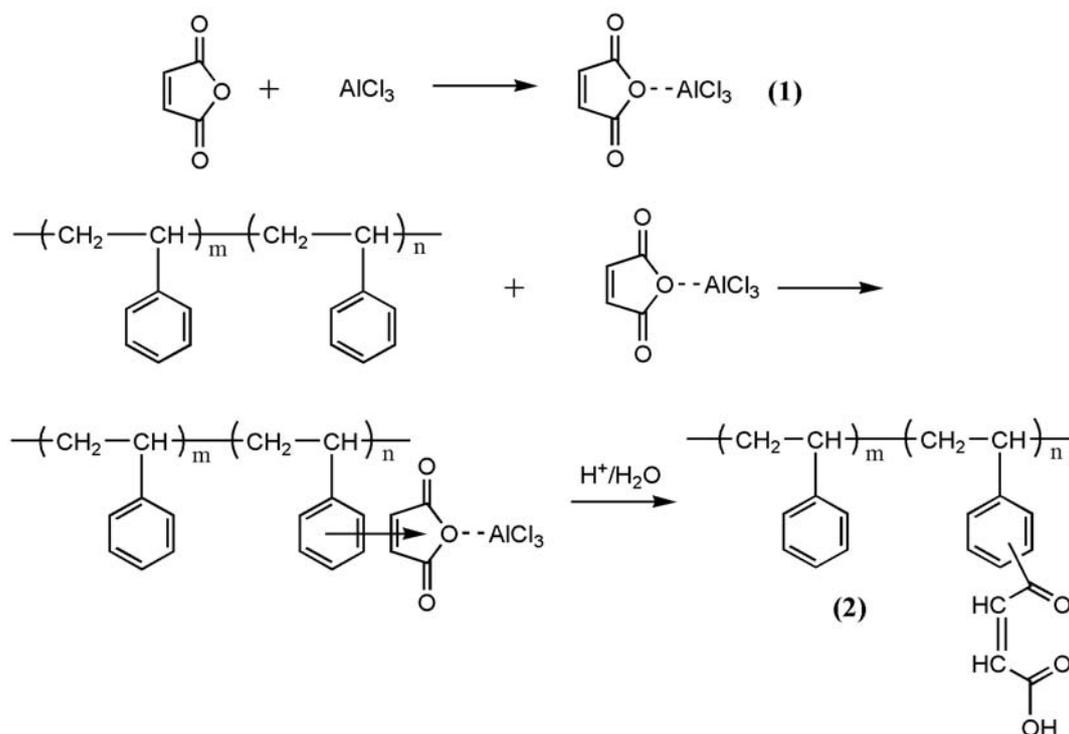
Quantitative analysis corresponding to the amount of pendant carboxyl groups incorporated onto sPS was performed by a titration method as follows: 0.20 g of modified polymer was put in 50 mL refluxing chloroform/methanol mixture (99/1, v/v) for 2 h. Then the hot solution was directly titrated to a phenolphthalein end-point using sodium hydroxide (0.050 M) in methanol. Results were expressed as the content of carboxyl groups, which is defined as the mole percentage of the maleated styrene units. Sample without modification was also titrated, yielding the blank value.

Thermal analysis was performed using a TA instruments Q10 differential scanning calorimeter equipped with a RCS accessory under nitrogen atmosphere. For all samples, the standard procedure is as follows: the samples (about 5 mg) were heated at 300°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 50°C to record the crystallization temperatures, and then reheated to 300°C to record the melting temperatures, all at a rate of 20°C.min<sup>-1</sup>. The recorded temperatures were calibrated using Indium as standard.

## RESULTS AND DISCUSSION

### Acylation Reaction

In this study, Friedel-Crafts acylation reaction was used to prepare m-sPS in a heterogeneous process. However, conducting this reaction in a solution state was proved to be difficult, since sPS only dissolves in high-boiling chlorinated solvents, such as 1,2,4-trichlorobenzene and 1,1,2-trichloroethane, at elevated temperatures. It is well known that chlorinated solvents and high temperatures will have opposite influence on the acylation procedure. Thus the synthesis of m-sPS is performed in a heterogeneous state using carbon disulphide as dispersing agent, MA as acylating agent and  $AlCl_3$  as catalyst. Firstly, a charge-transfer complex is formed between  $AlCl_3$  and MA in



**Scheme I.** Synthetic procedure of m-SPS.

carbon disulphide. After stirring this complex at about 25°C for 2 h, powder sPS (200 mesh) was added, then HCl formation took place and the polymer was functionalized (Scheme I). The following parameters, such as the amount of  $\text{AlCl}_3$ , reaction temperature and reaction time, were changed in order to optimize the process. The work-up procedure involves treatment with ice water followed by dilute hydrochloride acid to decompose the complex and dissolve the aluminium salts.

The effects of reaction conditions on the contents of carboxyl groups of m-SPS were investigated. The content of carboxyl groups, defined as the mole percentage of the acylated styrene units, was determined by chemical titration, and the data are presented in Table 1. The results show that in a certain range, an increase in the content of carboxyl groups can be observed with increasing the concentration of  $\text{AlCl}_3$ , elevating the reaction temperature and prolonging the reaction time. Furthermore, as shown in Table 1, the reaction temperature and the concentration of  $\text{AlCl}_3$  play an important role on the content of carboxyl groups in the Friedel-Crafts reactions. When MA and  $\text{AlCl}_3$  were first added as to form a charge-transfer complex in the reaction medium to eliminate undesir-

able side reactions, cross-linking was still observed in the presence of high levels of  $\text{AlCl}_3$ , i.e.,  $[\text{AlCl}_3]/[\text{MA}]$  molar ratio above 3/1, in parallel with high reaction temperature, i.e., above 25°C. For example, the mass percentage of cross-linked polymer increased from about 3% to 16% with prolonging the reaction time from 2 h to 4 h at a

**Table 1.** Synthesis of m-SPS by Friedel-Crafts reaction<sup>a</sup>.

Run	$[\text{AlCl}_3]$ (mmol)	Time <sup>b</sup> (h)	Temperature (°C)	DA <sup>c</sup> (mol%)
1	10	2	15	1.0
2	10	2	25	2.2
3	10	2	30	5.2
4	10	2	35	7.6
5	15	2	25	4.0
6	20	2	25	6.2
7	15	4	25	4.5

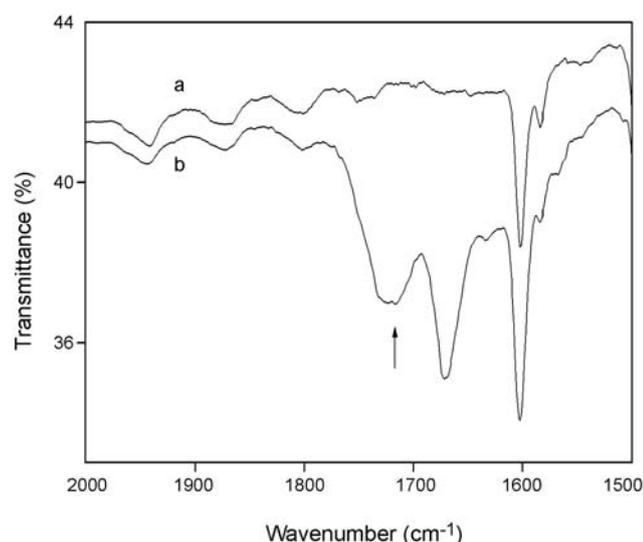
(a) Conditions: sPS, 0.52 g (5.0 mmol); MA, 0.49 g (5.0 mmol);  $\text{CS}_2$ , 50 mL; (b) The reaction time is referred to duration of reaction between the  $\text{AlCl}_3$ -MA charge-transfer complex and sPS polymer; (c) DA is referred to the content of carboxyl groups (mol%) obtained by titration analysis.

[AlCl<sub>3</sub>]/[MA] molar ratio of 2/1. Similarly, if the reaction time was fixed within 2 h, the cross-linked polymer was found to increase from about 3% to 12% when [AlCl<sub>3</sub>]/[MA] molar ratio was increased from 2/1 to 3/1. The results indicate that a relatively higher equimolar catalyst concentration, which depends on the [AlCl<sub>3</sub>]/[MA] molar ratio is desired to promote functionalization efficiency. This is attributed to a low reactivity between MA and AlCl<sub>3</sub> generated on the sPS backbone, which is believed to be responsible for the increased cross-linking.

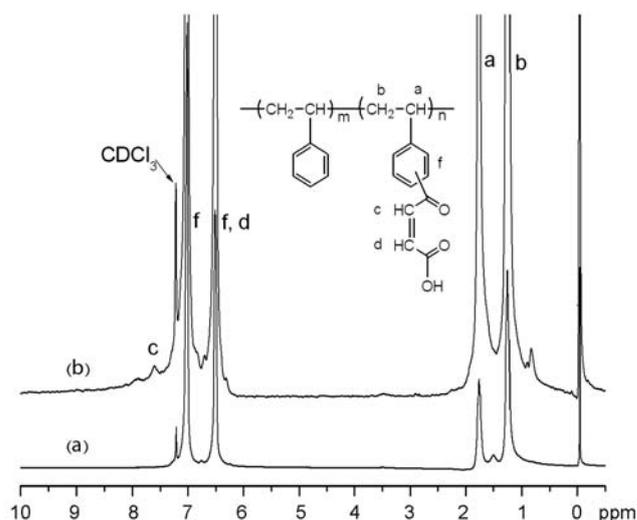
### Characterization

To aid in the structural elucidation of the MA-functionalization chemistry, sPS with carboxyl moieties along the backbone was analyzed using FTIR spectroscopy, and assignments for the characteristic groups were developed.

FTIR spectra of pure sPS and m-sPS with the content of carboxyl groups of 4.5 mol% in the range of 2000-1500 cm<sup>-1</sup> are given in Figures 1a and 1b, respectively. Compared with Figure 1a, two new bands appeared at 1670 cm<sup>-1</sup> and 1720 cm<sup>-1</sup> in Figure 1b, which confirmed the presence of carboxyl groups in the modified sPS. In addition, two different carbonyl groups separated by carbon-carbon double bond in the m-sPS molecule can be assigned to individual keto and acid groups. Conjugation with an



**Figure 1.** FTIR spectra of pure sPS (a), and m-sPS (b) with carboxyl groups content of 4.5 mol% in the range of 2000-1500 cm<sup>-1</sup>.



**Figure 2.** <sup>1</sup>H NMR spectra (a) pure sPS, and (b) m-sPS with carboxyl groups content of 4.5 mol%.

aromatic group and a carbon-carbon double bond leads to a lower frequency, thus the keto absorbs at 1670 cm<sup>-1</sup>, while the acid exhibits absorbance at 1720 cm<sup>-1</sup> due to isolated and hydrogen-bonded carboxyl groups [20]. In addition, a new peak at 1635 cm<sup>-1</sup> is contributed to the absorbance of the double bond in the functional moieties.

Supporting evidence for the structural elucidation was revealed by <sup>1</sup>H NMR analysis. Figure 2 shows the <sup>1</sup>H NMR spectra of starting sPS and m-sPS with the content of carboxyl groups of 4.5 mol%. The resonances at about 1.8 and 1.3 ppm are assigned to CH and CH<sub>2</sub> units in the sPS backbone, respectively. After modification, the protons for MA groups were appeared at 6.6 and 7.6 ppm. In addition, a new peak due to the protons *ortho* to the substituted group appeared around 7.9 ppm in the aromatic region. A similar chemical shift was observed for the published succinoylated sPS [16]. In addition, the undetectable resonance of the protons in the -COOH may be due to the formation of hydrogen bonding between inter- or intra-molecules.

From the results of infrared and NMR spectroscopic analysis, it can be deduced that the modified sPS contains -COCH=CHCOOH groups in side phenyl rings. That is to say, Friedel-Crafts acylation of sPS with MA can introduce both carboxyl groups and double bonds onto pendant aromatic groups of the polymer. This situation is quite different from the MA

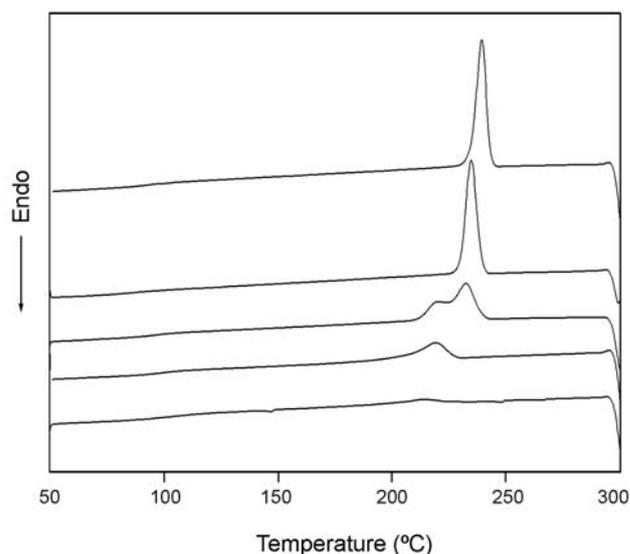
grafted sPS prepared by a radical process, in which MA attaches to the sPS aliphatic backbone in the form of single succinic anhydride rings as well as short oligomers as reported previously by our group [7]. In addition, degree of functionalization obtained by the free radical-induced method, i.e., 1.2 wt%, is much lower than that prepared by Friedel-Crafts reaction.

### Thermal Analysis

In attempt to understand the link between the incorporation of functional groups and the crystallization of m-sPS, the thermal behaviour of m-sPS was investigated by means of DSC.

The sample subjected to the DSC experiments were used according to the following protocol: equilibrium at 300°C and kept at this temperature for 5 min, then cooling from 300°C to 50°C, and finally reheating from 50°C to 300°C, both heating and cooling rates are 20°C.min<sup>-1</sup>. Figures 3 and 4 exhibit DSC scans of sPS (a) and related m-sPS with different contents of carboxyl groups (b) 0.7 mol %, (c) 1.3 mol %, (d) 4.0 mol % and (e) 7.6 mol %. Table 2 lists the thermal data for each of the samples shown in Figures 3 and 4.

In the cooling scans of the samples (Figure 3), the crystallization endotherm of pure sPS occurs at the highest crystallization temperature ( $T_c$ ) and has the sharpest crystallization exotherm, while  $T_c$  and enthalpy of crystallization ( $\Delta H_c$ ) for m-sPS samples from the melt decreased with increasing the content of carboxyl groups. Furthermore, a more broadened transition temperature has been observed for all



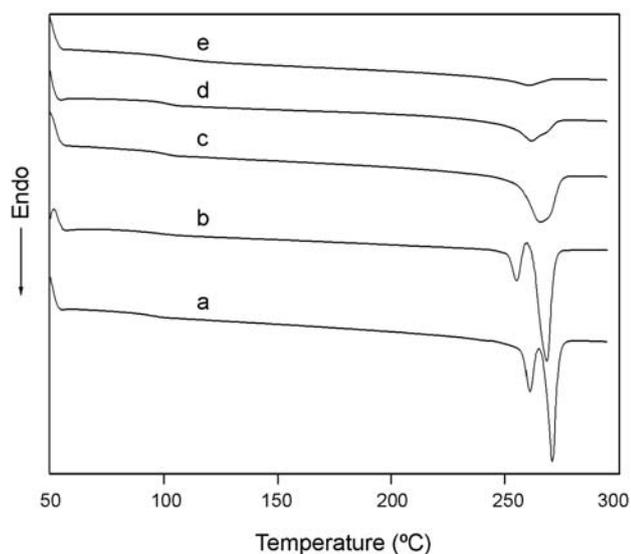
**Figure 3.** DSC cooling scans of (a) pure sPS and m-sPS with different contents of carboxyl groups (mol%), (b) 0.7 , (c) 1.3 , (d) 4.0, and (e) 7.6.

maleated samples and the transition temperatures become broader with increasing the content of carboxyl groups, which indicates that the non-isothermal crystallization rate decreases with increasing the content of carboxyl groups. This suggests that the crystallization rate can be retarded by the presence of covalently attached carboxyl groups. For the 7.6 m-sPS sample, it is unable to crystallize during the cooling scan from 300°C to 50°C at a cooling rate of 20°C.min<sup>-1</sup>. This may be attributed to the cross-linking of double bond during heating, which shows larger impact in comparison to that of succinoylated sPS

**Table 2.** Summary of DSC results for sPS and m-sPS.

Run	DA <sup>a</sup> (mol%)	$T_g^b$ (°C)	$T_m^b$ (°C)	$\Delta H_m$ (J.g <sup>-1</sup> )	$X_c^c$ (%)	$T_c^b$ (°C)	$\Delta H_c$ (J.g <sup>-1</sup> )
a	0.0	92.7	270.7	29.5	55.7	239.5	30.4
b	0.7	96.9	268.3	32.8	61.9	234.7	29.4
c	1.3	101.4	265.4	23.7	44.7	232.5	23.6
d	4.0	101.4	261.5	13.9	26.2	219.0	11.3
e	7.6	103.2	260.3	3.9	7.4	212.7	1.2

(<sup>a</sup>) DA is referred to the content of carboxyl groups (mol%); (<sup>b</sup>) The glass transition temperatures,  $T_g$ s, were determined as the mid-point of the step change in the heat flow. The melting,  $T_m$ , and crystallization,  $T_c$ , temperatures were selected as the peak maximum or minimum in endothermic or exothermic transition, respectively; (<sup>c</sup>) The degree of crystallinity,  $X_c$ , is determined by the equation:  $X_c = (\Delta H_m / \Delta H_m^0) \times 100\%$ , where  $\Delta H_m$  is the melting enthalpy of the sample and  $\Delta H_m^0$  is the melting enthalpy of 100% crystalline sPS (53 J.g<sup>-1</sup>).



**Figure 4.** DSC heating scans of (a) pure sPS and m-SPS with different contents of carboxyl groups (mol%); (b) 0.7; (c) 1.3; (d) 4.0; and (e) 7.6.

(still exist crystalline exotherm peak) [16].

Generally, the degree of crystallinity ( $X_c$ ) of crystallizable polymer materials can be estimated by measuring the enthalpic changes at melt. The melting enthalpy of 100% crystalline sPS has been reported to be  $53 \text{ J.g}^{-1}$  [21]. The data in Table 2 exhibits a systematic trend of  $X_c$  depression with increasing the content of carboxyl groups. For the sample with content of carboxyl groups of 7.6, its  $X_c$  value is 7.4%, much lower than that of neat sPS (56%).

The melting point ( $T_m$ ) of maleated polymers in Figure 4, as expected, exhibits a systematic trend of depression as increasing the content of carboxyl groups. The  $T_m$  of neat sPS is around  $270^\circ\text{C}$ , similar to the value previously obtained. For the 7.6 maleated polymer sample,  $T_m$  decreases to about  $260.3^\circ\text{C}$ . This result is quite different from the acetylated syndiotactic polystyrene [14]. For the 42.6 mol% acetylated syndiotactic polystyrene sample,  $T_m$  is about  $265^\circ\text{C}$ . This phenomenon may be explained by comparing the size of acyl substituents between the acylated styrenic units. It is expected that in m-SPS due to the larger size of the substituent groups, the chain mobility, which is required for crystallization, would be lower compared to the acetylated sPS. Thus, based on this chain mobility argument, the maleated styrene units may interrupt or retard crystal growth, limiting the

size of the crystallites achievable and resulting in the depression of melting point.

The glass transition temperature ( $T_g$ ) data also helps in understanding the effects of functional groups on the movement of the polymer chains. It is clear from Table 2 that the  $T_g$  value of the modified polymer increases with increasing the content of carboxyl groups. For example, as the content of carboxyl groups increases,  $T_g$  increases from  $93^\circ\text{C}$  for neat sPS to  $103.2^\circ\text{C}$  for the 7.6 mol% m-SPS sample. As mentioned above, the substituent groups result in reducing the mobility of the polymer chains and therefore raising  $T_g$  values. Furthermore, compared with neat sPS, due to the interactions between the acid groups, e.g., hydrogen bonding, the mobility of the polymer chains is also reduced, thus raising  $T_g$  in the modified samples.

## CONCLUSION

In this paper, a feasible synthetic route for preparing maleated sPS was confirmed and the optimum condition was developed. Maleated syndiotactic polystyrene was accomplished by Friedel-Crafts reaction in a heterogeneous process by using carbon disulphide as dispersing agent, maleic anhydride as acylating agent and aluminium chloride as catalyst. An optimum reaction should be carried out at  $25^\circ\text{C}$  with a molar ratio of aluminium chloride to maleic anhydride of 2/1. The maleated syndiotactic polystyrene was confirmed by FTIR and  $^1\text{H}$  NMR spectroscopies. DSC results showed that the thermal behaviour of the maleated syndiotactic polystyrene exhibits considerable differences in comparison to the neat sPS. The melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), and degree of crystallinity of the maleated polymers decrease with increasing the content of carboxyl groups, while the glass transition temperature increases. This suggests that the crystallization behaviour can be retarded by the presence of covalently attached carboxyl groups.

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