

## Characterization and Dual Functionalization of Polystyrene with Propionic Anhydride and Cyanate Derivatives

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**ABSTRACT:** First, Friedel–Crafts reactions were used for the acylation process. For this, polystyrene (PS) was reacted with propionic anhydride in the presence of Lewis acid catalyst. The amount of acyl group linked PS as a result of acylation has been identified as volumetric. Second, the bromination and lithiation reactions of acylated PS containing carbonyl groups were realized. Also, the lithiated PS containing acyl groups has been modified a second time with various isocyanates and isothiocyanate derivatives in the presence of *n*-BuLi catalyst. Some important reaction parameters were assigned in order to optimize the process. The structure all of the products were characterized by Fourier transform infrared, <sup>1</sup>H NMR (Proton Nuclear Magnetic Resonance), and thermogravimetric methods. In addition, reaction yields were determined according to the result of elemental analysis. Dual functionalization yields were realized between 62.2% and 69.9%. For kinetic analysis, the TG/DTG (Thermal Gravimetric Analysis/Differential Thermal Analysis) data obtained at three different heating rates were processed by Kissinger–Akahira–Sunose method. The results demonstrated that the acylation reaction, bromination and lithiation reactions, and dual functionalization reactions with cyanate derivatives can be carried out to obtain a significantly functionalized polymer. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1351–1362, 2013

**KEYWORDS:** functionalization of polymers; thermal properties; polystyrene

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### INTRODUCTION

Polystyrene (PS) is a very attractive polymer because of its low specific gravity, low dielectric constant, high melting point, high modulus of elasticity, and excellent resistance to chemicals. Accordingly, it has become a promising material for various applications in the automotive, electronics, and packaging industries, too.<sup>1,2</sup> Aside from its wide use in industrial applications, PS is also used for the production of plastic materials, which are used instead of metals in technology.<sup>3</sup> However, PS without additional functional groups has limited properties such as thermal stability, mechanical strength, adhesion capability, corrosion resistance, and photosensitivity. The undesired properties of PS can be improved with different reagents using modification reactions.<sup>4–14</sup> The synthesis of new polymeric materials can be carried out by either the polymerization of new monomers or the chemical modification of polymers with an appropriate technique.<sup>15,16</sup> With the chemical modification, substances that have high molecular weights react chemically, like the low ones, and new kinds of polymers can be synthesized.<sup>5</sup> The preparation of polymers carrying various functional groups is a problem that has received much attention, as evidenced by the large body of literature devoted to this subject.<sup>17–21</sup> One of the most important reactions in the functionalization

of PS can subsequently be transformed into numerous other functional groups.<sup>22</sup> Two important steps in the functionalization of PS, bromination and lithiation, have been described in a previous report from this laboratory, and a number of functional polymers have been prepared from lithiated PS.<sup>22–24</sup> Many derivatives of PS are synthesized from poly-*p*-lithiumstyrene. The reason for this is because poly-*p*-lithiumstyrene with high molecular weight is a metal organic compound and shows similar features as metal organic compounds with low molecular weight according to the capable reaction.<sup>25</sup> A large number of reactions can be used to affect the chemical modification of polymers, but in a number of cases, the reactions are accompanied by undesired side reactions and the functional yields are low. Since the functional polymers cannot be purified once they have been prepared, it is desirable to use very simple systems in the functionalization reactions to avoid all side reactions whenever possible. Functionalization of PS containing organolithium reagents affords one the opportunity to modify the PS and incorporate additives which are chemically attached to the polymer.

The lithiation of PS has been studied by many researchers.<sup>21–34</sup> First, the lithiation of PS developed by Braun<sup>25</sup> involved the reaction of a solution of halogenated PS with an excess of *n*-

butyllithium. The reaction was usually carried out on substrates obtained by polymerization of *p*-iodostyrene. A number of workers have used the method developed by Braun and prepared polystyryllithium intermediates by the two-step bromination–lithiation procedure.<sup>20,29,31–34</sup> A comparison of the bromination–lithiation versus direct lithiation procedure would therefore indicate that the two-step lithiation is probably the method of choice if control of the position of lithiation and of the degree of functionalization is desired, since predictable results can be obtained in the bromination over a very broad range of degrees of functionalization; in addition, since the resin is fully swollen during the bromination, a more even distribution of the functional groups can be expected.<sup>22</sup> To test the reactivity of the polystyryllithium resin and explore its application to the preparation of PS resins containing various functional groups such as cyanate, a number of reactions were studied by Farrall and Frechet<sup>22</sup> and Leavitt.<sup>24</sup> Functionalized resins have found numerous applications recently as supports in solid-phase synthesis, reagents, or protecting groups in organic synthesis and supports for chromatography or catalysis.<sup>22</sup>

Previously, we have reported the chemical modification of PS with cyclic anhydrides by Friedel–Crafts reactions. The products were resistant to heat, impact, and various substrates and could be used as polymeric plate materials.<sup>4–8</sup> On continuing our studies on PS, we report here acylation, bromination, and lithiation reactions performed by electrophilic substitution reaction on the aromatic ring of PS and additional reactions between cyanate derivatives with poly-*p*-lithiumstyrene obtained as a result of these reactions.

The purpose of the present study is to investigate the reactions of lithiated PS containing the acyl group with cyanate derivatives in the presence of *n*-BuLi catalyst, thus to obtain new functionalized PSs containing two different functional groups (Figure 4) and to characterize products by Fourier transform infrared (FT-IR), <sup>1</sup>H NMR spectroscopies, and elemental and thermal analysis. The purpose is also to investigate the kinetics of thermal degradation of dual functionalized PS in argon under non-isothermal conditions, and also to investigate how the functional groups bonded to the aromatic rings of the PSs affect their properties. The improvement of industrial applications of PS with chemical modification is investigated in detail.

## EXPERIMENTAL

### Materials

PS was purchased from Aldrich ( $M_w = 2.3 \times 10^5$ ), and it was dissolved in benzene followed by precipitating in methanol and used after drying under vacuum at 50°C.  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  was purchased from Merck, and it was purified by distillation at 123°C. Tetrahydrofuran (THF) was dried by distillation in the presence of NaH at 66°C. Chloroform was dried overnight with calcium chloride, filtered, and distilled before use. Acylated polystyrene (AcPS) was prepared according to the previously published procedure.<sup>4</sup> Cyclohexylisocyanate (CHIC) and ethylisocyanate (EIC) were purchased from Aldrich; phenylisothiocyanate (PITC), cyclohexylisothiocyanate (CHITC), and ethylisothiocyanate (EITC) were purchased from Alfa Aesar; *n*-BuLi and propionic anhydride (PA) were purchased from

Across; and bromine, iodine, methyl alcohol, acetone, dichloromethane, and toluene were purchased from Merck, and all were used as-received.

### General Procedure for Bromination of AcPS

Synthesis of brominated styrene was as follows: 5.66 g (0.05 mol) of AcPS and 90 mL of  $\text{CH}_2\text{Cl}_2$  were mixed in a two-necked flask at 20°C for 30 min. Then, 7.62 g (0.03 mol) of  $\text{I}_2$  used as a catalyst was added to the mixture, and it was stirred for 30 min. Then, 3 mL (0.06 mol) of  $\text{Br}_2$  in 10 mL  $\text{CH}_2\text{Cl}_2$  solvent was added to the mixture, and it was stirred for 3 h. Reaction was performed under reflux. Brominated acyl polystyrene (Br-AcPS) was precipitated with methanol from the reaction mixture. Precipitated Br-AcPS was solved with 40 mL  $\text{CH}_2\text{Cl}_2$  and was extracted with KI solution to remove unreacted bromine. Br-AcPS was reprecipitated with methanol from the reaction mixture, filtered, washed with methanol at room conditions, and then dried under vacuum at 70°C for 5 h.

### General Procedure for Dual Functionalization with Cyanate Derivatives of Br-AcPS

Dual functionalization of brominated styrene was as follows: 1.53 g (10 mmol) of Br-AcPS and 70 mL of THF were mixed in a three-necked flask at 20°C for 30 min. Liquid nitrogen was added on a Dewar vessel with acetone in it; then, temperature was fixed in  $-78^\circ\text{C}$ , and the reaction was made under nitrogen in this Dewar vessel. Then, 4 mL (10 mmol) of *n*-BuLi in 5 mL THF solvent was added dropwise to the mixture at  $-78^\circ\text{C}$  under nitrogen, and it was stirred for 1 h. Afterward, 10 mmol isocyanate and isothiocyanate derivatives (EITC, EIC, CHITC, CHIC, PITC) in 5 mL THF solvent were added dropwise to the mixture at  $-78^\circ\text{C}$  under nitrogen, and it was stirred for 2 h. Dual functionalized AcPSs with isocyanate and isothiocyanate derivatives [AcPS-EITC (DFPS-1), AcPS-EIC (DFPS-2), AcPS-CHITC (DFPS-3), AcPS-CHIC (DFPS-4), AcPS-PITC (DFPS-5)] were precipitated with methanol from the reaction mixture. Precipitated dual functionalized AcPS were filtered, washed with methanol at room temperature, and then dried under vacuum at 70°C for 5 h.

### Measurements and Analyses

FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100. Film samples were cast in aluminum 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. <sup>1</sup>H NMR spectra were recorded at 25°C on a Varian 400 NMR spectrometer. Samples for <sup>1</sup>H NMR spectroscopy were prepared by dissolving about 20 mg of products in 1 mL deuterated chloroform. Tetramethylsilane was used as an internal reference. Thermogravimetric analysis (TGA) experiments were carried out by the use of Seteram thermogravimetric analyzer which was calibrated over all heating rates, using a gas purge, under the same conditions as those of the analysis. Polymer samples of about 10 mg were heated in a platinum crucible at 750°C using heating rates of 10, 15, and 20°C  $\text{min}^{-1}$  with a controlled argon flow of 50  $\text{cm}^3 \text{min}^{-1}$ .  $T_g$  was determined by a Perkin-Elmer DSC. The samples were measured from 25°C to 500°C in argon at a scanning rate of 10°  $\text{min}^{-1}$ . The CHNS-

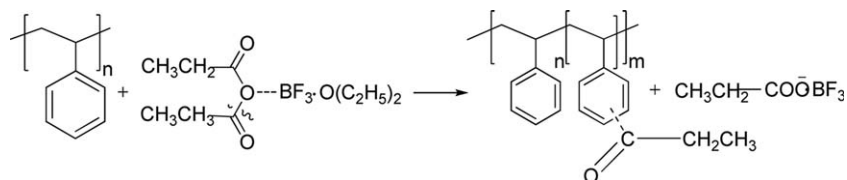


Figure 1. Friedel–Crafts acylation reaction of PS with PA.

932 Model LECO Elemental Analyzer was used for the determination of C, H, and N contents in the dual functionalized PSs.

#### Kissinger–Akahira–Sunose Method

The Kissinger–Akahira–Sunose (KAS) method<sup>35–37</sup> was based on the following equation:

$$\ln \frac{\beta}{T_x^2} = \ln \left[ \frac{AR}{E_a g(\alpha)} \right] - \frac{E_a}{RT_x}$$

The  $E_a$  at different conversion values can be calculated from the linear plots of

$$\ln \left[ \frac{\beta}{T_x^2} \right] \text{ versus } \frac{1}{T}$$

#### Chemical Analysis

**Determination of Propanoyl ( $-\text{COCH}_2\text{CH}_3$ ) Groups.** The concentration of the propanoyl group, connected to the structure of PS, was calculated by the titration of propionic acid with 0.1N KOH, which occurred after the chemical modification reaction of PS with PA by using  $\text{BF}_3(\text{C}_2\text{H}_5)_2$  as a catalyst.

$$\text{PA (mol/L)} = \frac{(\Delta V \times T_{\text{KOH}} \times 1000)}{56.1}$$

where PA is the concentration of the reacted PA,  $\Delta V$  is the volume used for the titration of propionic acid in the 1 mL sample (mL),  $T_{\text{KOH}}$  is the amount of KOH in 1 mL 0.1N KOH solution (0.005608 g), and 56.1 g is the molecular weight of KOH.

## RESULTS AND DISCUSSIONS

### Acylation Reaction

Friedel–Crafts acylation reactions are aromatic substitution reactions 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  $\text{AlCl}_3$ <sup>38</sup> and  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ .<sup>4,5</sup> These reactions are widely used to modify PS through the side groups (phenyl rings) of macromolecules.<sup>39</sup> In this study, first, Friedel–Crafts acylation reaction was used to prepare AcPSs. The bonding reaction of PA to the aromatic ring of the polymer with  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  is shown in Figure 1. According to the chemical analysis, it was determined that one acyl group was connected to one of each of the six aromatic rings of PS. The degree of acylation corresponding to the amount of propionic acid that occurred in acylation reaction was determined by chemical titration.

### Bromination Reaction

Bromination of PS containing acyl group which was obtained from acylation reactions with PA of PS was made according to the literature (Figure 2 and 3).<sup>34</sup> Bromination reaction of PS was carried out by Friedel–Crafts reactions using electrophilic bromine, which were obtained from the reaction between bromine and iodine (Figure 3). As a result of this reaction, bromine was connected to the p-positions of the aromatic rings which is not found in the acyl group of AcPS.<sup>33</sup>

### Lithiumation Reaction and Dual Functionalization

Lithiumation reaction of brominated PS containing acyl group and second-time functionalization of PS were reacted at  $-78^\circ\text{C}$  in the presence of *n*-BuLi used as a catalyst. Electrophilic substitution reaction with brominated AcPS of lithium and the reactions with cyanate derivatives of poly-p-lithiumstyrene were made under the same reaction conditions (run 2 in Table I).

Xue et al.<sup>33</sup> report definitive evidence on the lithiation which shows that only a hydrogen atom on the ring of PS is replaced. The reaction at this site is a consequence of the kinetic and thermodynamic acidity of the polymer. They also explained that this is not a surprising result and that direct lithiation of the benzene ring occurs, and lithiation of PS occurs only at the p-position, not at the benzylic position.<sup>33</sup> Reaction mechanism with isocyanate and isothiocyanate derivatives of Br-AcPS is given as follows.

As shown in Figure 4, first, poly-p-lithiumstyrene with acyl group containing lithium in the aromatic ring was obtained from electrophilic substitution reaction with *n*-BuLi of PS with acyl group containing bromine in the aromatic ring. Second, salt of poly-p-lithiumstyrene containing amid group was obtained by participation of the reaction on double bond in between carbon–nitrogen [ $-\text{N}=\text{C}=\text{O}(\text{S})$ ] in the cyanate derivatives with poly-p-lithiumstyrene acting as a Lewis acid. In the last step, the modified PSs containing the amide, thioamide, and acyl group were obtained by treating the corresponding poly-p-lithiumstyrene salts with HCl.

The effects of various parameters such as the amount of *n*-BuLi, cyanate derivatives, and Br-AcPS, and reaction time on

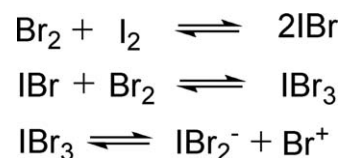
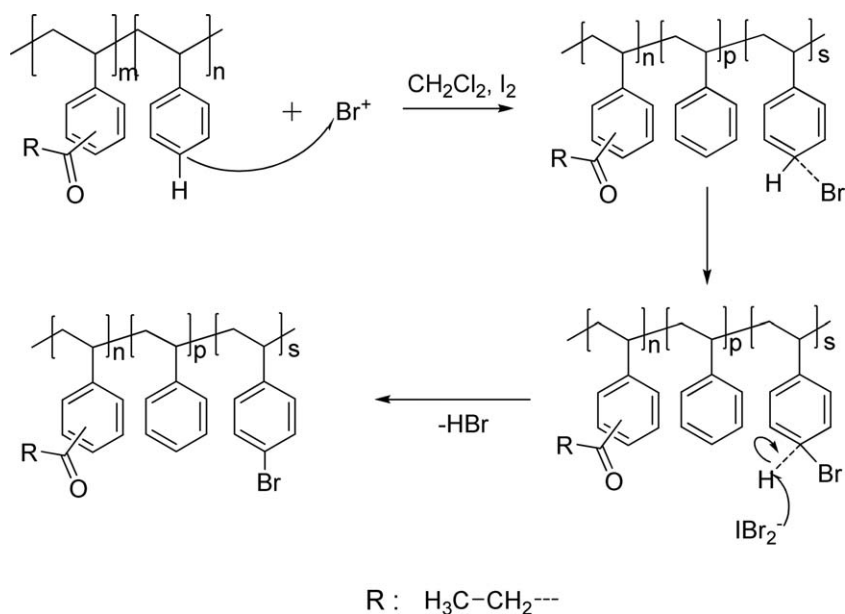


Figure 2. Bromine as an electrophile been obtained.



**Figure 3.** Reaction mechanisms with bromine of AcPS.

the reaction were determined. The results obtained from the second functionalization reaction of Br-AcPS with EIC in the presence of *n*-BuLi are given in Table I.

As shown in Table I, the optimum reaction condition is as follows: a ratio of EIC to Br-AcPS is 1/1 (mol/mol), a ratio of Br-AcPS to *n*-BuLi is 1/1 (mol/mol), and 2 h of time under reflux and in nitrogen atmosphere. The results indicate that a significant change in the amount of second-time functionalization has been observed initially with increasing *n*-BuLi concentration. A relatively higher amount of *n*-BuLi (up to optimum *n*-BuLi amount) which depends on the amount of *n*-BuLi is desired to promote second functionalization yield. Increasing *n*-BuLi amount more did not show a significant change in second functionalization yield. The equivalent amount of cyanate derivatives was equal to that of Br-AcPS under optimum reaction

conditions. Under optimum reaction conditions, according to chemical elemental analysis results, it was determined that the second functional group was connected to three of each of the aromatic rings of PS. The second-time functionalization reaction of Br-AcPS was also carried out using EITC, EIC, CHITC, CHIC, and PITC. Their reactions were conducted under optimum conditions as in run 2 (see Table I).

The number of repetition of the second functional group connected to the aromatic ring of PS from % nitrogen amount as a result of elemental analysis is as follows (Figure 5).

For example, consider the product obtained by the reaction between EIC and PS containing acyl group, where *n* is the AcPS, *p* is the unmodified PS, and *s* is the second-time functionalized PS.

**Table I.** Second Functionalization with EIC of Br-AcPS

Run	Br-AcPS/ cyanate <sup>a</sup> (mol/mol)	<i>n</i> -BuLi/Br-AcPS (mol/mol)	Time (h)	( <i>n</i> : <i>p</i> : <i>s</i> ) <sup>b</sup>	% N	Second functionalization yield (%)
1	1 : 1	1 : 1	1	1 : 2.99 : 2.01	2.740	33.58
2 <sup>c</sup>	1 : 1	1 : 1	2	1 : 1.85 : 3.15	4.868	52.40
3	1 : 1	1 : 1	3	1 : 1.89 : 3.11	4.772	51.90
4	1 : 1	0.5 : 1	2	1 : 3.30 : 1.70	2.635	28.36
5	1 : 1	0.75 : 1	2	1 : 2.60 : 2.40	3.717	40.01
6	1 : 1	2.5 : 1	2	1 : 1.90 : 3.10	4.802	51.67
7	1 : 1	2 : 1	2	1 : 1.92 : 3.08	4.785	51.54
8	0.5 : 1	1 : 1	2	1 : 2.70 : 2.30	3.568	38.40
9	1 : 1.5	1 : 1	2	1 : 1.95 : 3.05	4.732	50.93

<sup>a</sup>EIC.

<sup>b</sup>Ratio of contents of PS (*p*) to AcPS (*n*) and to dual functionalized PS (*s*) units in macromolecules.

<sup>c</sup>The optimum values of the reaction is presented in run 2.

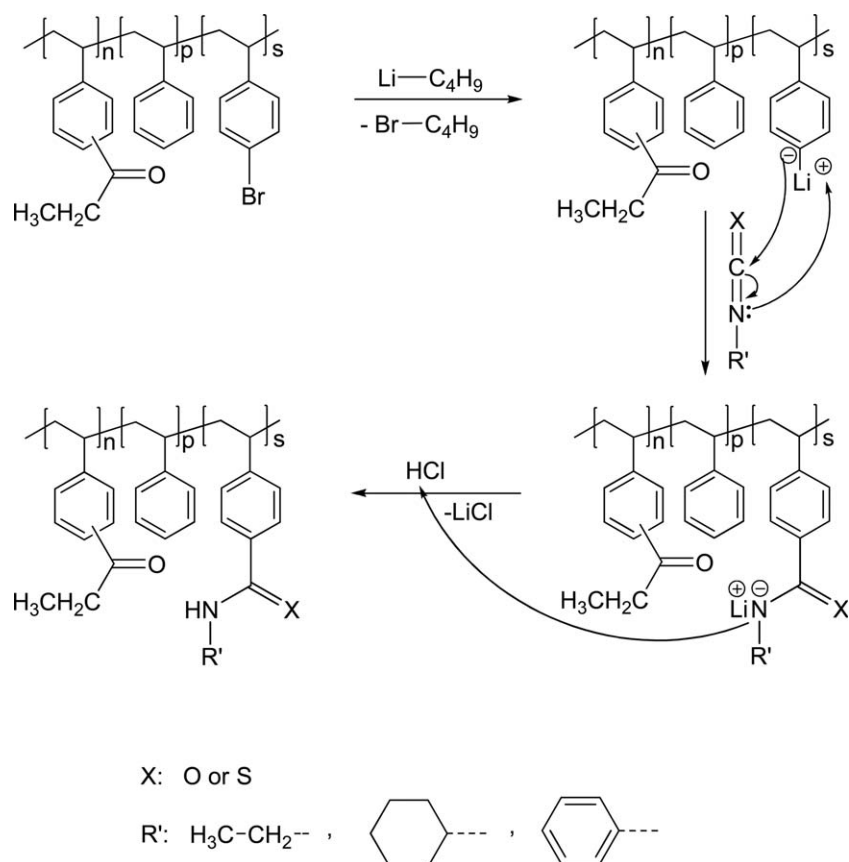


Figure 4. Reaction mechanisms with isocyanate and isothiocyanate derivatives of Br-AcPS.

According to the results of chemical analysis; $p = 1$ and $(n + p) = 5$	
where $s = x$ we say, $n = (5 - x)$ .	
Total molecular weight	: $[104 \times (5 - x)] + 160 + 176x$
	: $680 + 72x$
Total nitrogen weight	: $14x$
$14x$ , in $680 + 72x$ , if,	
there are 4.868 nitrogen units in 100 units (Table II)	
$(680 \times 4.868) + (72x \times 4.868) = 1400x$	
$1049.5x = 3310.2$	
$x = 3.15 \cong 3 = s$	

Approximately, the second functional group connected to three of the six aromatic rings of PS were determined.

Accordingly, PS connected to three amide groups and one acyl group in the six aromatic rings was obtained. Two of the aromatic rings are not connected to any group. The amount of modification groups in the polystyrene chain was approximately determined as  $n : p : s = 1 : 2 : 3$ , respectively, according to the results of elemental analysis.

All cyanate derivatives used in the second functionalization reaction gave around 50% efficiency. The second functionalization group has been connected to approximately three of each of the

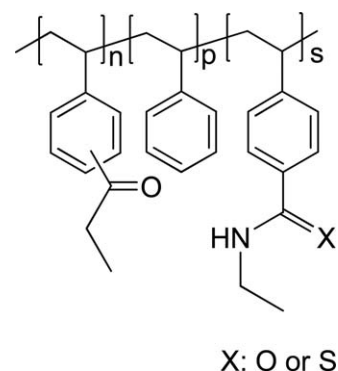


Figure 5. The numbers of repetition of dual functionalized PS.

six aromatic rings (see Table II). The highest dual functionalization yield was obtained with EIC and the lowest yield with CHITC and PA. Under optimum reaction conditions, the results showed that between 62% and 69% of aromatic rings of PS have been modified with both PA and cyanate derivatives (see Table II).

#### FT-IR Analysis

FT-IR was the first spectroscopic tool we used to identify successful acylation of the PS with PA and second-time functionalization with isocyanates and isothiocyanates of AcPS. The FT-IR spectra of PS (A), AcPS (B), DFPS-1 (C), DFPS-2 (D), DFPS-3 (E), DFPS-4 (F), and DFPS-5 (G) are given in the range of

**Table II.** Characterization of Second Functionalization with Cyanates of Br-AcPS

Run	Polymers	Cyanates	% N	Second Functionalization Yield (%)	Dual Functionalization Yield (%)	(n : p : s) <sup>a</sup>
1	AcPS	-	-	-	-	(m : n) <sup>b</sup> 1 : 5
2	DFPS-1	EITC	4.244	46.6	63.3	1 : 2.20 : 2.80
3	DFPS-2	EIC	4.868	52.4	69.1	1 : 1.85 : 3.15
4	DFPS-3	CHITC	3.587	45.5	62.2	1 : 2.27 : 2.73
5	DFPS-4	CHIC	4.026	50.8	67.5	1 : 1.95 : 3.05
6	DFPS-5	PITC	3.789	48.2	64.9	1 : 2.10 : 2.90

<sup>a</sup> Ratio of contents of PS (p) to AcPS (n) units and to dual functionalized PS (s) units in macromolecules.

<sup>b</sup> Ratio of contents of PS (m) to AcPS (n) units in macromolecules.

3500–600  $\text{cm}^{-1}$  in Figure 6(a–g), respectively. By comparing the above seven spectra, it is clear that new bands, which are absent in the spectrum of the PS (trace a) and the AcPS (trace B), can be ascertained in the spectra of the second-time functionalization with isocyanates and isothioisocyanate of AcPS (traces c–g).

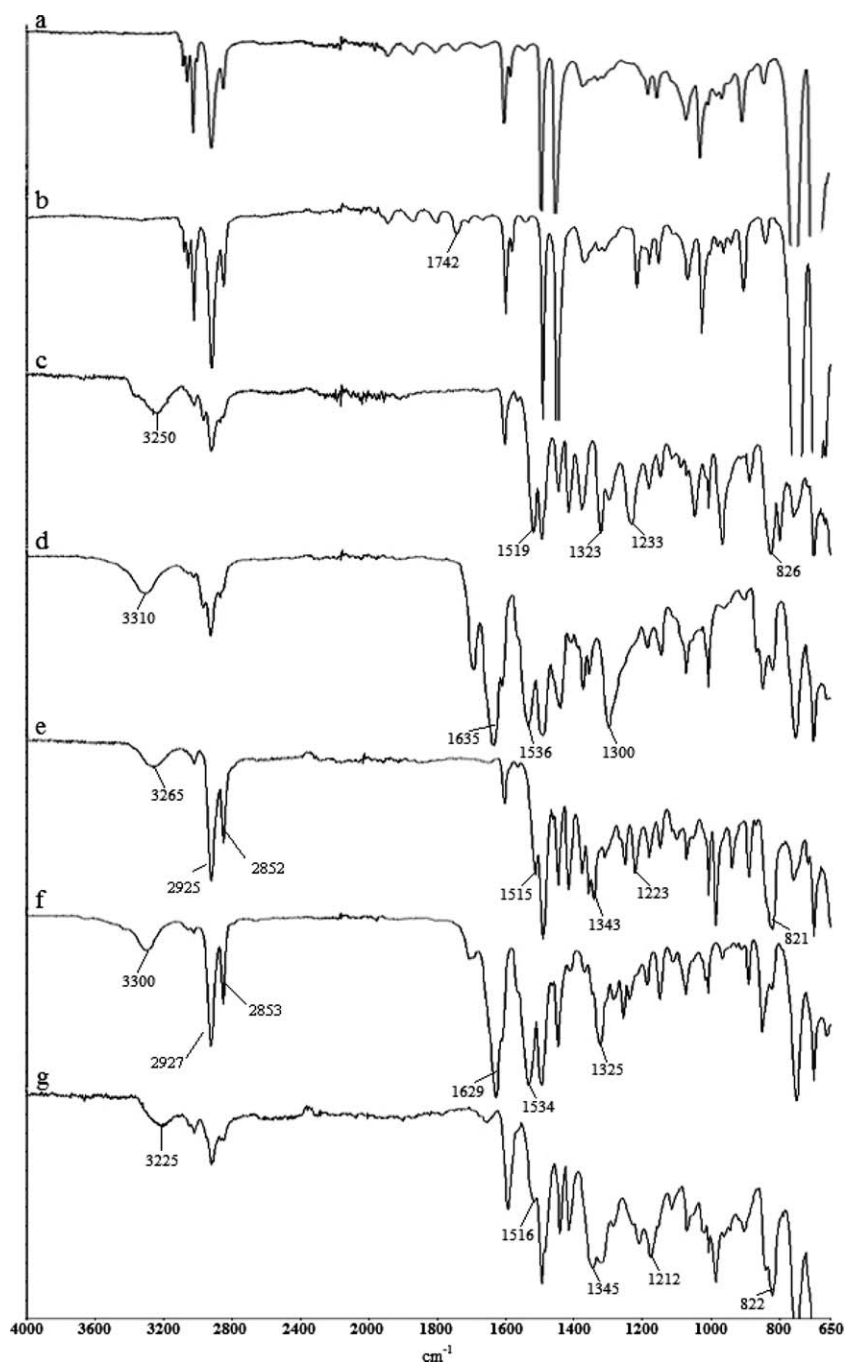
In the FT-IR spectra of the AcPSs with PA, the band appeared at 1742  $\text{cm}^{-1}$  was ascribable to carbonyl groups of individual ketone (trace b). The bands appeared at 3250  $\text{cm}^{-1}$  was ascribable to a broad peak contributing to (–CS–NH) group stretching vibration. Also, a new peak at 1519  $\text{cm}^{-1}$  was ascribable to –NH bending motion combined with a –CN stretching vibration of the [C(=NH)–NH–] group (thioamide I); a peak at 1323  $\text{cm}^{-1}$  was ascribable to (–N–C=S) (thioamide II) and the introduction of the thioamide group into the fibrous sorbent is verified by (C=S) stretching vibration; and peaks at 1233–826  $\text{cm}^{-1}$  were ascribable to thioamide III and IV; (trace c). The bands appeared at 3310  $\text{cm}^{-1}$  was ascribable to a broad peak corresponding to (O=C–NH) group N–H stretching vibration secondary amide. Also, a new peak at 1635  $\text{cm}^{-1}$  was assigned to the stretching vibration of the C=O bond from amide groups, an amide I band; a band at 1536  $\text{cm}^{-1}$  was ascribable to N–H deformation-amide II band; and a band at 1300  $\text{cm}^{-1}$  was ascribable to (–CN) amide III band (trace d). The bands appeared at 3265  $\text{cm}^{-1}$  was ascribable to a broad peak contributing to (–CS–NH) group stretching vibration. Also, a new peak at 1515  $\text{cm}^{-1}$  was ascribable to –NH bending motion combined with a –CN stretching vibration of the [C(=NH)–NH–] group (thioamide I), a peak at 1343  $\text{cm}^{-1}$  was ascribable to (–N–C=S) (thioamide II) and the introduction of the thioamide group into the fibrous sorbent is verified by (C=S) stretching vibration; and peaks at 1223–821  $\text{cm}^{-1}$  were ascribable to thioamide III and IV, and also, because of –cyclohexyl group in 2925 and 2852  $\text{cm}^{-1}$  peak, intensity increased (trace e). The bands appeared at 3300  $\text{cm}^{-1}$  was ascribable to a broad peak contributing to (O=C–NH) group N–H stretching vibration secondary amide. Also, a new peak at 1629  $\text{cm}^{-1}$  was assigned to the stretching vibration of the C=O bond from amide groups, an amide I band; a band at 1534  $\text{cm}^{-1}$  was ascribable to N–H deformation-amide II band; and a band at 1325  $\text{cm}^{-1}$  was ascribable to (–CN) amide III band, and also, because of cyclohexyl group in 2927 and 2853  $\text{cm}^{-1}$  peak, intensity

increased (trace f). The bands appeared at 3225  $\text{cm}^{-1}$  was ascribable to a broad peak contributing to (–CS–NH) group stretching vibration. Also, a new peak at 1516  $\text{cm}^{-1}$  was ascribable to –NH bending motion combined with a –CN stretching vibration of the [C(=NH)–NH–] group corresponding to (thioamide I); peak at 1345  $\text{cm}^{-1}$  was ascribable to (–N–C=S) (thioamide II) and the introduction of the thioamide group into the fibrous sorbent is verified by (C=S) stretching vibration; and peaks at 1212–822  $\text{cm}^{-1}$  were ascribable to (thioamide III and IV; trace g).

#### <sup>1</sup>H NMR Analysis

Supporting evidence for the structural elucidation was revealed by <sup>1</sup>H NMR analysis. Figure 7 shows the <sup>1</sup>H NMR spectra of PS (A), AcPS (B), DFPS-1 (C), DFPS-2 (D), DFPS-3 (E), DFPS-4 (F), and DFPS-5 (G).

Figure 7 displays the typical <sup>1</sup>H NMR spectrum of the unmodified PS (A) with four peaks around 1.6, 1.9, 6.6, and 7.2 ppm. After acylation with PA (B), two characteristic signals, around 2.6 ppm due to methylene (CH<sub>2</sub>) protons of –COCH<sub>2</sub>CH<sub>3</sub> moiety and about 1.4 ppm due to methyl (CH<sub>3</sub>) protons of –COCH<sub>2</sub>CH<sub>3</sub> moiety, were observed. In second-time functionalization with EITC of AcPS (C), three characteristic signals, around 1.2 ppm due to methyl (CH<sub>3</sub>) protons of –NHCH<sub>2</sub>CH<sub>3</sub> moiety, 3.6 ppm due to methylene (CH<sub>2</sub>) protons of –NHCH<sub>2</sub>CH<sub>3</sub> moiety, and 8.3 ppm due to (NH) protons of –NHCH<sub>2</sub>CH<sub>3</sub> moiety, are observed. In second-time functionalization with EIC of AcPS (D), three characteristic signals, around 1.25 ppm due to methyl (CH<sub>3</sub>) protons of –NHCH<sub>2</sub>CH<sub>3</sub> moiety, 3.9 ppm due to methylene (CH<sub>2</sub>) protons of –NHCH<sub>2</sub>CH<sub>3</sub> moiety, and 8.9 ppm due to (NH) protons of –NHCH<sub>2</sub>CH<sub>3</sub> moiety, were observed. In second-time functionalization with CHITC of AcPS (E), three characteristic signals, around 1.2–2.1 ppm due to methylene (CH<sub>2</sub>) protons of (–cyclohexyl) moiety, 3.9 ppm due to methine (CH) protons of [–NH–CH (in cyclohexyl)] moiety, and 8.4 ppm due to (NH) protons of (–NH–cyclohexyl) moiety, were observed. In second-time functionalization with CHIC of AcPS (F), three characteristic signals, around 1.2–2.2 ppm due to methylene (CH<sub>2</sub>) protons of (–cyclohexyl) moiety, 4.5 ppm due to methine (CH) protons of [NH–CH (in cyclohexyl)] moiety, and 9.1 ppm due to (NH) protons of (–NH–cyclohexyl) moiety, were observed. In second-

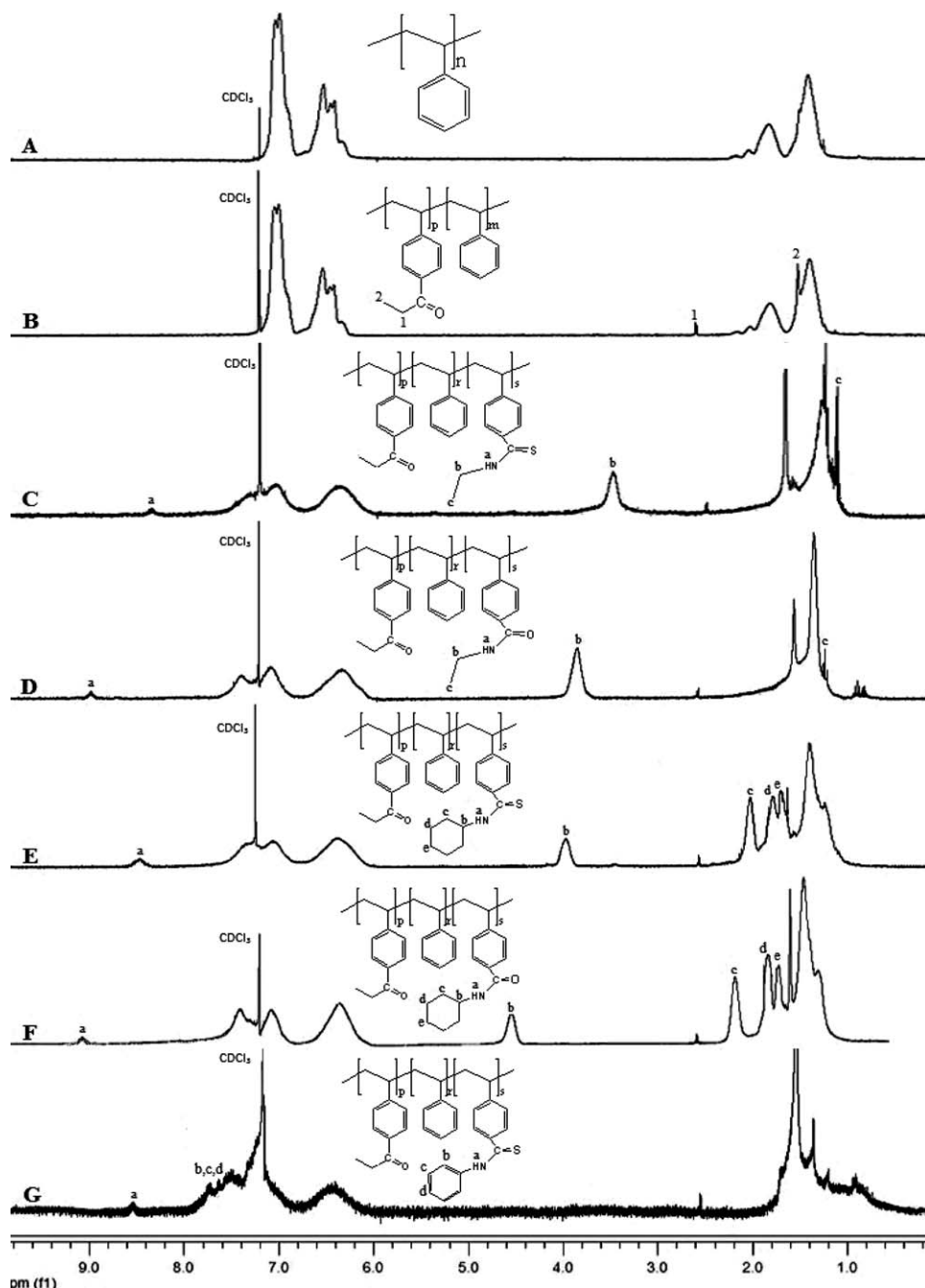


**Figure 6.** FT-IR spectra of PS (a), AcPS (b), DFPS-1 (c), DFPS-2 (d), DFPS-3 (e), DFPS-4 (f), and DFPS-5 (g) in the range 3500–600  $\text{cm}^{-1}$ .

time functionalization with PITC of AcPS (G), two characteristic signals, around 7.6–7.9 ppm methine (CH) protons of phenyl moiety and 8.5 ppm due to (NH) protons (NH-phenyl) moiety, were observed. By comparing the above five  $^1\text{H}$  NMR spectra (C–G), it is clear that signals were observed at 3.5–4.5 ppm due to methylene ( $-\text{CH}_2$ ) and methine ( $-\text{CH}$ ) protons in the spectrum of the  $^1\text{H}$  NMR spectra of C–F compounds, but they were not observed in the spectrum of the  $^1\text{H}$  NMR spectra of G compound. These new peaks sufficiently prove that second-time functionalization of AcPS reactions occurred.

### Thermal Analysis

The thermal degradation is very important process, which helps to know the influence of the polymer structure on the thermal stability, the temperature at which the polymers can be used, and the activation energy associated with the total degradation process. Literature reports several papers on thermal properties of styrene polymers.<sup>40–45</sup> Also, there are some reports available in literature<sup>46–49</sup> that discuss improving the thermal stability of certain categories of polymers, which is carried out with a chemical modification of their structure by introducing active

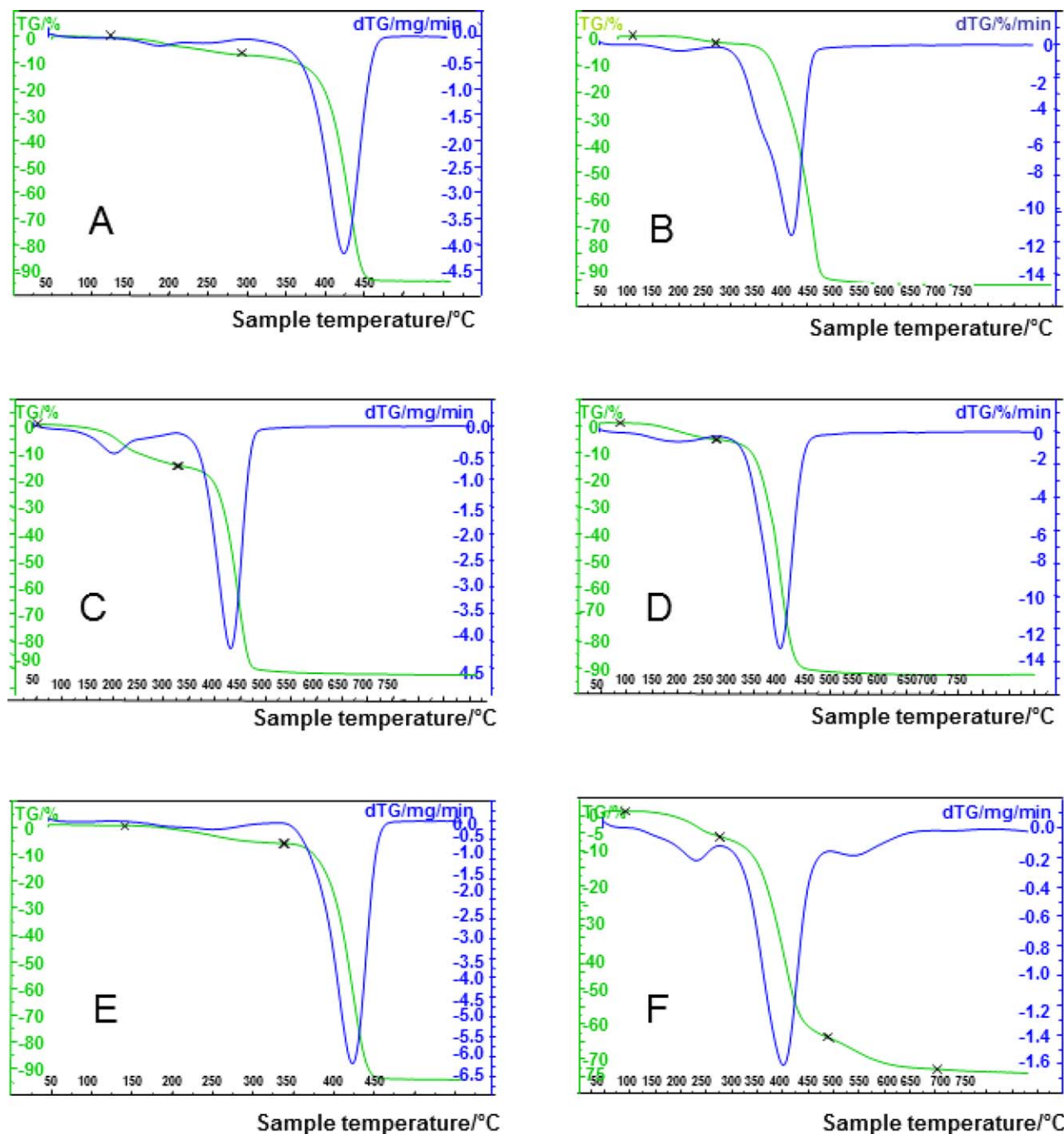


**Figure 7.**  $^1\text{H}$  NMR spectra of PS (A), and AcPS (B), DFPS-1 (C), DFPS-2 (D), DFPS-3 (E), DFPS-4 (F), and DFPS-5 (G).

functional groups (e.g., isocyanates, thioureas, and carbamates). In previous works, we determined that PS modified by various modifiers has more stability against thermal destruction than unmodified PS,<sup>6–8</sup> depending on the structure and amount of active functional groups bound to the aromatic ring. In our study, thermal behaviors of the AcPS and dual functionalized AcPS with cyanate derivatives were investigated by TGA in the temperature range of 50–750°C. Their TGA, DTG, and DTA curves are shown in Figure 8. PS shows one weight loss stage over 350°C, while TGA curves of AcPS and dual functionalized AcPS with cyanate derivatives show two stages. Initial

degradation for AcPS and dual functionalized PSs with cyanate derivatives was in the range of 140–225°C for AcPS, 140–275°C for DFPS-1, 150–325°C for DFPS-2, 140–275°C for DFPS-3, 150–325°C for DFPS-4, and 140–275°C for DFPS-5. The second-stage degradation temperature of all modified polymers was above 350°C. The products of the second stage are the typical aromatic materials which arise from the degradation of PS.<sup>50</sup> Styrene was the major product of degradation, and the most important minor products were benzene, ethyl benzene, and toluene.<sup>51</sup> In DTG curves of all modified polymers, two minima at the temperatures between 200 and 220°C and between 425





**Figure 8.** TG–DTG curves of AcPS and PS dual functionalized with cyanates [AcPS (A), DFPS-1 (B), DFPS-2 (C), DFPS-3 (D), DFPS-4 (E), and DFPS-5 (F)]. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and 445°C were appeared. The observed endothermic peaks demonstrate that melting and decomposition occurred together. Both modified PSs are very stable against thermal destruction and have similar weight loss with PS up to 380°C. But, at the temperature above 380°C, thermal resistance of dual functionalized PSs was higher than in PS. The degradation in the first stage of dual functionalized PSs may correspond to amide and acyl groups bound PS, lead to the formation of carbon dioxide, amines, carbon monoxide, etc. In the second stage at about

380–425°C, the degradation may be due to the aromatic materials which arise from the degradation of modified PS.

Effect of anchoring carbonyl and isocyanate (isothiocyanate) groups on PS was investigated thermally for AcPS and dual functionalized PS with cyanate derivatives (Table III). In AcPS and dual functionalized PS with cyanate derivatives, weight loss at 140°C was 3%, unlike unmodified PS.<sup>8</sup> It may be due to the functional groups bound to the aromatic ring of PS. The

**Table III.** Thermal Properties of PS, AcPS, and PSs Second Functionalized with Isocyanates and Isothiocyanates

Polymers	Loss of Weight (%)					Residual Weight (%)	$T_g$ (°C)
	140°C	350°C	380°C	425°C	450°C	≥500°C	
Unmodified PS <sup>b</sup>	–	6	21	81	98	0	105
AcPS	3	4	6	70	97	2	175
DFPS-1	3	6	20	62	92	5	197
DFPS-2	3	13	20	58	93	5	199
DFPS-3	3	7	23	67	93	5	198
DFPS-4	3	7	21	68	92	5	201
DFPS-5	3	8	24	55	68	20	202

55–68% weight loss was at 425°C for dual functionalized PSs and 70% weight loss at 425°C for AcPS. However, the 81% weight loss was at 425°C for the unmodified PS.  $T_g$  of the unmodified PS and AcPS was observed as 105°C and 175°C, respectively, while  $T_g$  of dual functionalized PSs was between 197°C and 202°C. Thus, it was determined which thermal stability of dual functionalized PS was more stable than those of both AcPS and unmodified PS (Table III).

The derivation of kinetic data of polymer decomposition by TGA can be used to determine the rate constants, activation energies, reaction order, and Arrhenius pre-exponential factors.<sup>52</sup> The method for the evaluation of kinetic parameters for thermal decomposition has been reviewed by several researchers many times.<sup>53</sup> The activation energy for the decomposition of these polymers was evaluated using the well-known KAS method. The thermal stability and decomposition process of these dual functionalized PSs (DFPS-1 and DFPS-2) have also been studied by the thermogravimetric technique to evaluate the activation energy by KAS method.<sup>35–37</sup> KAS method is used to determine the energy of activation ( $E_a$ ) at constant several conversion degrees ( $\alpha$ ; Table IV). The plots of  $\ln(\beta/T^2)$  versus  $1/T$  corresponding to conversion degrees ( $\alpha$ ) were constructed.

Figure 9 shows the TGA–DTG curves corresponding to the dual functionalized PSs (DFPS-1 and DFPS-2). A weak endothermic effect (at about 204.1°C, 205.3°C, and 207.2°C) followed by intense endothermic effect at about 425.2°C, 426.8°C, and

428.3°C was observed at different heating rates [(A) 10 K min<sup>-1</sup>, (B) 15 K min<sup>-1</sup>, and (C) 20 K min<sup>-1</sup>]. The weight losses of 92.3%, 92.6%, and 92.2% were observed at different heating rates (for DFPS-1). This total decomposition was accompanied by an endothermic effect with a maximum at 450°C, and the decomposition was completed after this period (for DFPS-1). And, also a weak endothermic effect (at about 211.4°C, 215.6°C, and 218.3°C) followed by intense endothermic effect at about 435.13°C, 438.15°C, and 443.22°C was observed at different heating rates [(D) 10 K min<sup>-1</sup>, (E) 15 K min<sup>-1</sup>, and (F) 20 K min<sup>-1</sup>]. The weight loss of 93.3%, 92.4%, and 92.6% were observed at different heating rates (for DFPS-2). This total decomposition was accompanied by an endothermic effect with a maximum at 465°C, and the decomposition was completed after this period (for DFPS-2). The results showed that DFPS-2 is more stable than DFPS-1, thermally (Figure 9).

Different heating rates gave different Arrhenius plots; therefore, a series of  $E_a$  values can be determined from the slopes of the straight lines at conversion degrees (Table IV). According to the KAS isoconversional method, straight lines with the angular coefficient  $-E/R$  were obtained, and then a series of  $E_a$  values can be calculated using equation (KAS). The average values of  $E_a$  in the range  $0.4 \leq \alpha \leq 0.7$  were found to be  $242.17 \pm 3.4$  kJ mol<sup>-1</sup> and  $291.70 \pm 9.1$  kJ mol<sup>-1</sup> for DFPS-1 and DFPS-2, respectively. According to the results, the activation energy of DFPS-2 was higher than that of DFPS-1 (Table IV).

**Table IV.** Activation Energies for DFPS-1 and DFPS-2

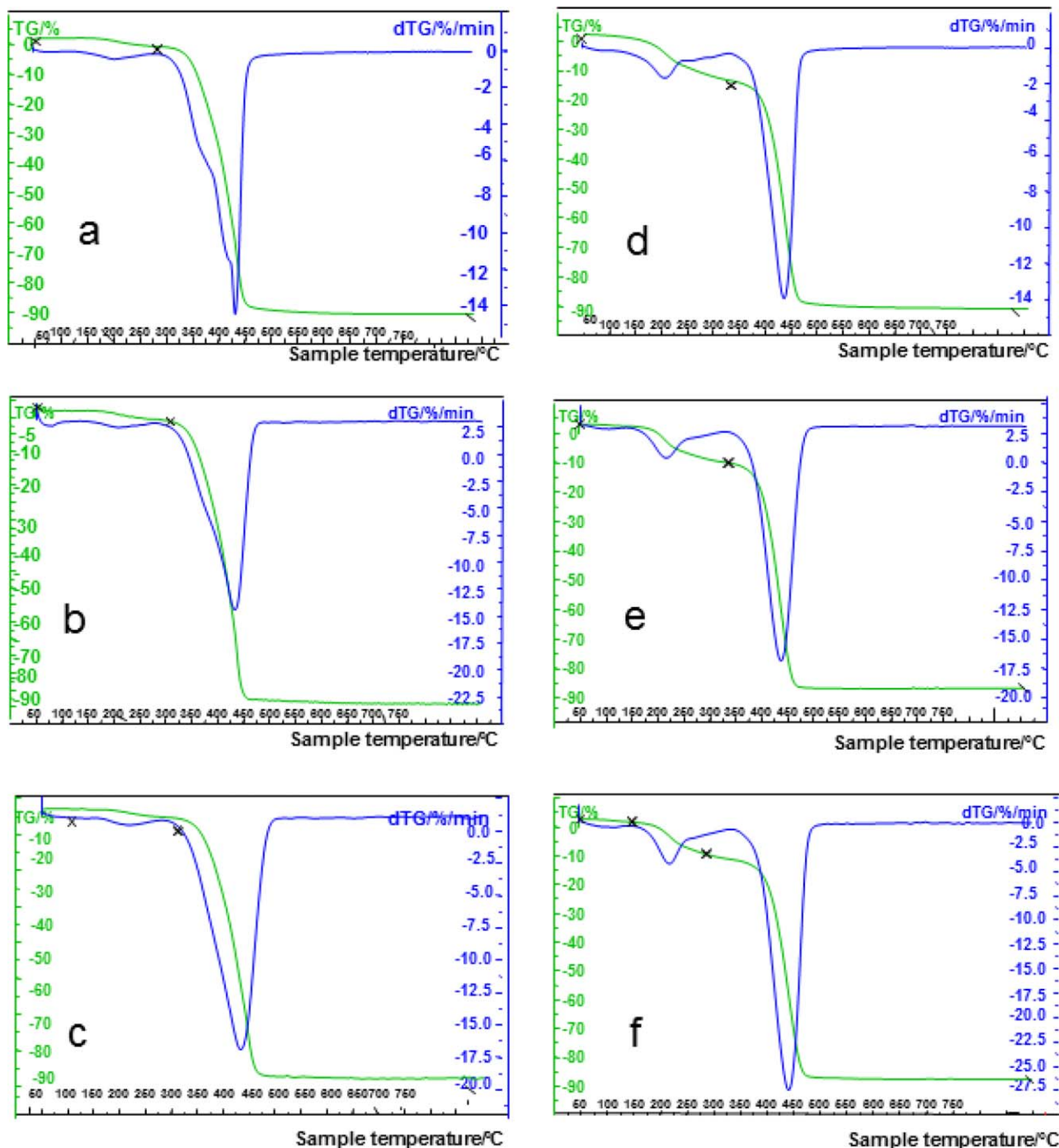
$\alpha^a$	Activation energy, <sup>b</sup> $E_a$ (kJ mol <sup>-1</sup> )	
	DFPS-1	DFPS-2
0.2	188.94	167.43
0.3	211.17	234.75
0.4	241.71	282.29
0.5	249.35	300.03
0.6	238.08	299.07
0.7	242.54	285.42
0.8	217.44	261.72

<sup>a</sup> Conversion degrees.

<sup>b</sup> Different heating rates (10 K min<sup>-1</sup>, 15 K min<sup>-1</sup>, and 20 K min<sup>-1</sup>).

## CONCLUSIONS

Dual functionalization of PS was accomplished using THF as a dispersing agent, cyanate derivatives as a second modifier agent, and *n*-BuLi as a catalyst. An optimum reaction should be carried out at -78°C having a molar ratio of cyanate derivatives to Br-AcPS of 1/1 (mol/mol), a ratio of Br-AcPS to *n*-butyl lithium of 1/1 (mol/mol), and 2 h of time under reflux and in nitrogen atmosphere. The structures of AcPSs were confirmed by FT-IR and <sup>1</sup>H NMR spectroscopies. Their thermal behaviors were analyzed by thermogravimetric methods. Dual functionalized PS enhanced its thermal stability. Dual functionalized yield was determined by elemental analysis. It was determined that second functional group is connected to three of the six aromatic rings of PS. All cyanate derivatives used in the second functionalization reaction gave around 50% efficiency.



**Figure 9.** TG curves of DFPS-1 at different heating rates [(A) 10, (B) 15, and (C) 20 K min<sup>-1</sup>] and of DFPS-2 [(D) 10, (E) 15, and (F) 20 K min<sup>-1</sup>] in argon atmosphere. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Thus, novel modified PS which contains dual functionalized groups was prepared. The functionalized PS offers possibility for the development of novel PS-based polymer blends and composites, thus extending the application field of PS.

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#### REFERENCES

1. Richard, C.; James, L. *Polymer Engineering Principles*, Hanser: Munich, 1993.
2. Skinner, S. J.; Baxter, S.; Gray, P. J. *Trans. Plast. Inst.* **1964**, *32*, 180.
3. Sayed, W. M. J. *Appl. Polym. Sci.* **2008**, *109*, 4099.
4. Onder, I. L.; Okudan, A. *Int. Polym. Process.* **2012**, *XXVII(2)*, 270.

5. Kurbanova, R. A.; Mirzaoglu, R.; Akovali, G.; Zakir, M. O. R.; Karatas, I.; Okudan, A. *J. Appl. Polym. Sci.* **1996**, *59*, 235.
6. Kurbanova, R. A.; Mirzaoglu, R.; Kurbanov, S.; Karatas, I.; Pamuk, V.; Ozcan, E.; Okudan, A.; Guler, E. *J. Adhes. Sci. Technol.* **1997**, *11*, 105.
7. Kurbanova, R. A.; Okudan, A.; Mirzaoglu, R.; Kurbanov, S.; Karatas, I.; Ersoz, M.; Ozcan, E.; Ahmedova, G.; Pamuk, V. *J. Adhes. Sci. Technol.* **1998**, *12*, 947.
8. Okudan, A.; Baktir, S.; Sagdic, A. *Adv. Polym. Technol.* **2012**, doi:10.1002/adv.21292.
9. Zinck, P.; Bonnet, F.; Mortreux, A.; Visseaux, M. *Prog. Polym. Sci.* **2009**, *34*, 369.
10. Bas, S. Z.; Yildirim, M.; Yildiz, S. *Mater. Plast.* **2012**, *49*(1), 15.
11. Kenyon, W. O.; Wough, G. P. *J. Polym. Sci.* **1958**, *32*, 83.
12. Swiger, R. T. *J. Polym. Sci.* **1975**, *13*, 1554.
13. Frechet, J. M. J.; de Smet, M.; Farrall, M. J. *Tetrahedron Lett.* **1979**, *20*(2), 137.
14. Dogan, F.; Kaya, I.; Dayan, O.; Ozdemir, E. *J. Appl. Polym. Sci.* **2007**, *106*, 3454.
15. Gaylord, N. G.; Mehta, R.; Kumar, V.; Taki, M. *J. Appl. Polym. Sci.* **1989**, *38*, 359.
16. Harrison, C. R.; Hodge, P.; Kemp, J.; Perry, G. M. *Macromol. Chem.* **1975**, *176*, 267.
17. Schofer, J. L.; Lipman, B. *Functionalization of polystyrene resins*, Pat. 4,463,135, **1984**.
18. Frechet, J. M. J.; Farrall, M. J. In *Chemistry and Properties of Crosslinked Polymers*; Labana, S. S., Ed.; Academic Press: New York, **1977**, p 59.
19. Gibson, H. W.; Bailey, F. C. *Macromolecules* **1976**, *9*, 10.
20. Gibson, H. W.; Bailey, F. C. *Macromolecules* **1976**, *9*, 688.
21. Gibson, H. W.; Bailey, F. C. *J. Polym. Sci. Polym. Chem. Ed.* **1974**, *12*, 2141.
22. Farrall, M. J.; Frechet, J. M. J. *J. Org. Chem.* **1976**, *41*, 3877.
23. Frechet, M. J.; Smet, M. D.; Farrall, M. J. *J. Org. Chem.*, **1979**, *44*, 1774.
24. Leavitt, F. C. *Preparation of lithium substituted polystyrene polymers*, Pat. 3,234,196, **1966**.
25. Braun, D. *Makromol. Chem.* **1959**, *30*, 85.
26. Evans, D. C.; Phillips, L.; Barrie, J. A.; George, M. H. *J. Polym. Sci. Polym. Lett. Ed.* **1968**, *12*, 649.
27. Evans, D. C.; George, M. H.; Barrie, J. A. *J. Polym. Sci. Polym. Lett. Ed.* **1968**, *12*, 247.
28. Chalk, A. J. *Polym. Lett.* **1968**, *6*, 649.
29. Camps, F.; Castells, J.; Fernando, M. J.; Font, J. *Tetrahedron Lett.* **1971**, 1713.
30. Moreto, J.; Albaiges, J.; Camps, F. *An. Quim.* **1974**, *70*, 638.
31. Weinshenker, N. M.; Crosby, G. A.; Wong, J. Y. *J. Org. Chem.* **1975**, *40*, 1966.
32. Crosby, G. A.; Weinshenker, N. M.; Uh, H. S. *J. Am. Chem. Soc.* **1975**, *97*, 2232.
33. Xue, T.; Jones, M. S.; Ebdon, J. R.; Wilkie, C. A. *J. Polym. Sci. Part. A: Polym. Chem.* **1997**, *35*, 509.
34. Cakmak, I.; Coskun, M. *Sci. Eng. J. Firat Univ.* **2005**, *17*(2), 455.
35. Kissinger, H. E. *Anal. Chem.* **1957**, *29*, 1702.
36. Kissinger, H. E. *J. Res. Nat. Bur. Stand.* **1956**, *57*, 217.
37. Akahira, T.; Sunose, T. *Res. Rep. CHIBA Inst. Technol.* **1971**, *16*, 22.
38. Andrew, S. J. *Introduction to Organic Chemistry*; New York: Wiley, **1971**.
39. Sun, G.; Chen, T. Y.; Worely, S. D. *Polymer* **1996**, *37*, 3753.
40. Lisa, G.; Avram, E.; Paduraru, G.; Irimina, M.; Hurduc, N.; Aelenei, N. *Polym. Degrad. Stab.* **2003**, *82*, 73.
41. Costa, L.; Camino, G.; Guyot, A.; Bert, M.; Clouet, G.; Brosas, J. *Polym. Degrad. Stab.* **1986**, *14*, 85.
42. Zeliazkow, M. S. *Polym. Degrad. Stab.* **2001**, *74*, 3, 579.
43. Zeliazkow, M. S. *Polym. Degrad. Stab.* **2006**, *91*, 1233.
44. Guthrie, J. T.; Percival, J. A. *Polymer* **1977**, *18*, 531.
45. Manikandan, N. K. C.; Thomas, S.; Groeninckx, G. *Compos. Sci. Technol.* **2001**, *61*, 2519.
46. Ogunniyi, D. S.; Hepburn, C. *Iran. J. Polym. Sci. Technol.* **1994**, *3*, 48.
47. Bechara, I. *J. Cell. Plast.* **1979**, *15*, 102.
48. Barikani, M.; Hepburn, C. *Cell. Polym.* **1986**, *6*, 169.
49. Yeganeh, H.; Barikani, M.; Khodabadi, F. N. *Iran. Polym. J.* **2000**, *9*(3), 249.
50. Suzuki, M.; Wilkie, C. A. *Polym. Degrad. Stab.* **1995**, *47*, 217.
51. Kurt, A.; Demirelli, K. *Turkish J. Sci. Technol.* **2009**, *4*, 65.
52. Carmeron, G. G.; Rudin, A. *J. Polym. Sci. Polym. Phys. Ed.* **1981**, *19*, 1799.
53. Dickens, B.; Flynn, J. H. *Polymer Characterization*, ed. C. Craver, Chap. 12, American Chemical Society, Washington D.C., **1983**, 203–232.