Post Sulfonation of Bisphenol A Poly(arylene ethers)

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ABSTRACT: In this study, bisphenol A polyetherimide (PEI) was sulfonated by a novel postsulfonation route using trimethylsilylchlorosulfonate. Different degrees of sulfonation were achieved by varying the mole ratio of the sulfonating agent to the PEI repeat unit and the reaction time. Comparison was made with respect to bisphenol A polysulfone (PSU) to study the influence of electron withdrawing group in the sulfonated poly(arylene ethers) (SPAE) backbone on sulfonation. Structural characterization of SPAE was conducted by ^{1}H-NMR and FTIR spectroscopy. The enhanced reaction rate with PSU compared to PEI was attributed to the deactivation of bisphenol A unit due to the stronger electron withdrawing effect of imide group. The sulfonation of PEI was also carried out with chlorosulfonic acid for comparative study. The effects of degree of sulfonation on thermal and mechanical properties of SPAE-s were studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and a tensile testing machine. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2514–2522, 2010

Key words: amorphous; functionalization of polymers; degradation; NMR

INTRODUCTION

The sulfonated polymers have received considerable interests in the last decade because of their wide variety of applications in electronics, medical and automotive industries. Extensive studies have addressed sulfonated poly(arylene ether) membranes as key component in electrochemical processes including fuel cells, batteries, chemical sensors, electrochromic displays, electrodialysis, chloro- alkali process etc. Sulfonated poly(phenylene oxide) and polysulfone (PSU) are widely used as desalination membranes for reverse osmosis and water purification.[1,2] Sulfonated poly(ether sulfones) and poly(etherimide) membranes have been reported to be useful in ultrafiltration.[3–6] A major drawback of the application is membrane fouling, which has been minimized by increasing hydrophilicity of the polymer through sulfonation. The water-soluble sulfonated polystyrene, with high degree of sulfonation is useful as thickeners and flocculants. The dyeability of propylene-styrene copolymer can be improved by sulfonation.[7] Sulfonated polyphenylsulfone has been claimed for applications as dental plaque barriers and in hemodialysis membranes, the hemocompatibility is directly related to the degree of sulfonation.[8,9]

Poly(arylene ethers) are a class of well known high performance engineering thermoplastics that possess high glass transition temperature, high thermal stability, high chemical resistance, excellent mechanical properties and high resistance to oxidation. There are many varieties of poly(arylene ethers) such as PSU, polycarbonate, poly(ether ketones), poly(ether imides).

In the literature, different postsulfonation routes to introduce sulfonic acid group in the poly(arylene ether) repeat units are available. Quentin[10] first reported the sulfonation of PSU by chlorosulfonic acid (CSA). Noshay and Robeson[11] utilized sulfur trioxide –triethyl phosphate complex (SO$_3$-TEP) to sulfonate PSU at room temperature. The level of sulfonation was controlled by the ratio of SO$_3$ to TEP. This mild sulfonating agent could minimize the undesirable side reaction to a greater extent. Although the modification method is less expensive, the reaction is exothermic and difficult to control due to the high reactivity and toxicity of sulfur trioxide.[12] A quantitative and regiospecific method of introducing sulfonic acid group was introduced by Kerres et al.[13] In this method, the polymer was reacted with *n*-butyllithium and then with sulfur dioxide (SO$_2$) followed by oxidation/hydrolysis. The process based on three successive steps – metalation– sulfination and oxidation was relatively complicated and difficult to control. Recently, another mild sulfonating agent, trimethylsilyl chlorosulfonate was used to sulfonate activated aromatic ring.[14–16]

The most important issues of a sulfonation route are the toxicity level of the sulfonating agent, homogeneity of the reaction medium, control on the sulfonation level and cost. The optimum degree of sulfonation for maximizing the performance of these materials in terms of mechanical and thermal properties is mostly desired. To date, sulfonation of

TABLE I
Sample Designations and Sulfonation Conditions of SPAE-s

Sample designation	Concentration of TMSCS x[a]	Conditions time (h)	Degree of sulfonation (DS)(%)	Ion exchange capacity (IEC) (meq/g)
SPEI(16)H	0.7	24	16	0.35
SPEI(18)H	0.7	48	18	0.39
SPEI(22)H	0.7	72	22	0.47
SPEI(34)H	1.1	24	34	0.72
SPEI(13)H	1.5	6	13	0.28
SPEI(48)H	1.5	24	48	0.98
SPEI(57)H	1.5	48	57	1.16
SPEI(62)H	1.5	72	62	1.25
SPEI(33)H	2	24	33	0.7
SPSU(10)H	0.3	24	10	0.21
SPSU(9)H	0.7	6	9	0.2
SPSU(23)H	0.7	24	23	0.49
SPSU(30)H	0.7	48	30	0.64
SPSU(32)H	0.7	72	32	0.69
SPSU(40)H	1.1	24	40	0.84
SPSU(40)H	1.5	6	40	0.85
SPSU(65)H	1.5	24	65	1.31
SPSU(70)H	1.5	48	70	1.4
SPSU(76)H	1.5	72	76	1.52
SPSU(57)H	2	24	57	1.17

[a] x is defined as number of moles of TMSCS per mole of polyarylene ether repeat unit.

polyetherimide (PEI) with CSA has been reported by few researchers.[17,18] In this article, for the first time, a controlled sulfonation route for bisphenol A PEI by using trimethylsilylchlorosulfonate (TMSCS) is described. Comparison was made with respect to bisphenol A PSU to study the influence of electron withdrawing group in the polyarylene ether backbone on sulfonation. Effect of reaction time and concentration of the sulfonating agent were also studied. Additionally, postsulfonation using two different sulfonating agents, CSA and the trimethylsilyl ester were compared to provide a better understanding on the probable degradation mechanism. The sulfonated poly(arylene ethers) (SPAE) were characterized in terms of their thermal and mechanical properties.

EXPERIMENTAL

PEI (ULTEM 1000) and PSU (UDEL[RM] P-1700) were supplied by GE Plastics and Solvay Advanced Polymers, L.L.C. respectively and both were dried at 130°C for 8–9 h under vacuum. TMSCS and CSA were purchased from Aldrich Chemical Co. Methylene Chloride was dried over molecular sieves before its use as sulfonation reaction medium. Dimethylacetamide (DMAc) was used without further purification.
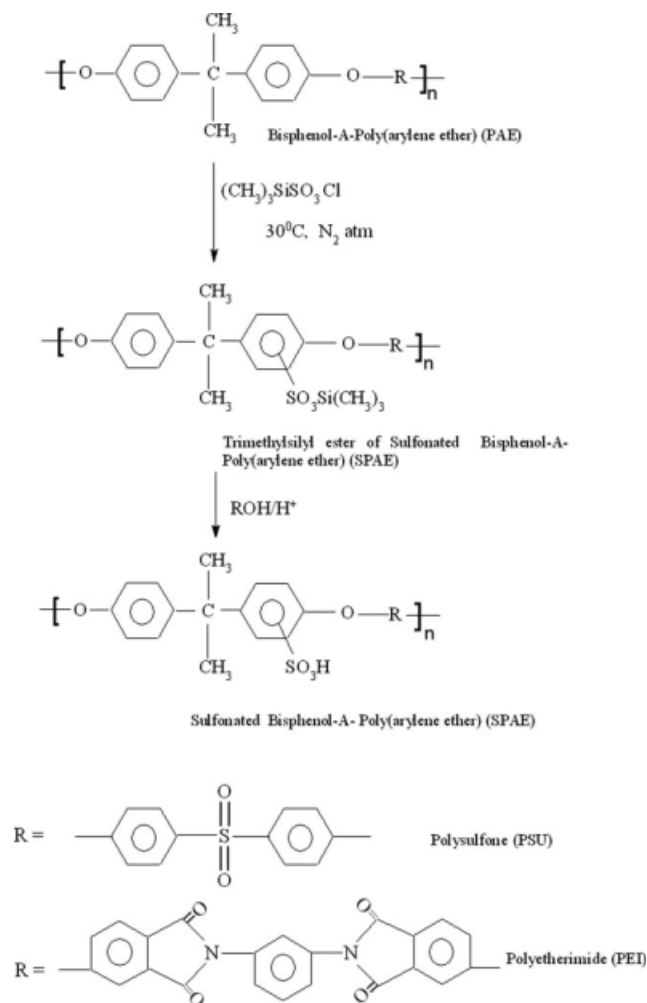
Sulfonation of bisphenol A poly(arylene ethers) (PAE)

Two bisphenol A poly(arylene ethers)-PEI and PSU were sulfonated by the procedure described below:

To a 250 mL, 3 necked round bottom flask fitted with a condenser, addition funnel and nitrogen sparge tube, 5 g of dried polymer was dissolved in 25 mL methylene chloride (~20% w/v solution). The solution was purged with nitrogen for one hour and TMSCS diluted in DCM was added slowly from a dropping funnel.The solution was stirred vigorously at ~30°C. The reaction mixture after the desired time was precipitated in acetone (sulfonated PEI) and methanol/isopropanol (sulfonated PSU depending on the degree of sulfonation). The fibrous precipitates were filtered, washed and dried. Sulfonated polyetherimide (SPEI) and polysulfone (SPSU) were dried under vacuum for 24 h at room temperature and 90°C respectively. Different degrees of sulfonation were achieved by varying the mole ratio of the sulfonating agent to the PAE repeat unit and/or the reaction time described in Table I. Sulfonated poly-(arylene ethers) were designated as SPAE(X)H, where X refers to degree of sulfonation. PEI was also sulfonated using CSA by the similar method for comparative study.

Characterization

The SPAE were characterized by ^{1}H nuclear magnetic resonance (NMR) and fourier transform infrared (FTIR) spectroscopy.The degree of sulfonation of SPAE was quantified by ^{1}H-NMR spectroscopy, recorded by Varian 300 MHz. All spectra was obtained from 1% (w/v) DMSO-d_6 solution at room temperature. FTIR spectroscopy of the SPAE

Scheme 1 Postsulfonation of poly(arylene ethers) by trimethylsilylchlorosulfonate.

samples was recorded in attenuated total reflection (ATR) mode using Nicolet 380 FTIR model. FTIR spectra of the samples were scanned in the absorbance mode from 4000 to 400 cm^{-1} with 32 scans and a resolution of 4 cm^{-1}.

Thermal degradation study of SPAE-s was performed using Thermal Advantage Q500 modulated thermogravimetric analyzer (TGA).The samples were heated from room temperature to 800°C at a heating rate of 10°C/min in nitrogen atmosphere.The thermal transition in SPAE-s was determined by TA 2920 Differential Scanning Calorimeter (DSC). The samples were heated from room temperature to 300°C at a heating rate of 10°C/min. All experiments were performed with 5–6 mg sample, sealed in aluminum hermetic pans under nitrogen atmosphere.

Viscosity measurements of SPAE-s were performed in DMAc solution using Ubbelohde capillary viscometer. The temperature was maintained at 35°C ± 2°C during the measurement. Tensile tests were carried out as per ASTM D 882 method using Instron 5567 tensile testing machine. The gauge length

and the width of the specimens were 25 and 5 mm respectively.

RESULTS AND DISCUSSION

Spectroscopic characterization of sulfonation by TMSCS

^{1}H-NMR

The sulfonation reaction of bisphenol A poly(arylene ether) is described in Scheme 1. Successful introduction of sulfonic acid group in the activated bisphenol A moiety of PEI is evident from ^{1}H-NMR spectra, shown in Figures 1 and 2. The spectra shows appearance of singlet at 7.79 ppm (e) corresponding to the protons adjacent to the sulfonic acid group and two doublets at 6.98 (i,j) and 7.88 ppm (f,g) associated with the sulfonated bisphenol A unit as depicted in Figures. It is clear that the peak intensity increases with increasing degree of sulfonation.The chemical shift positions of SPAE-s are shown in Table II. It was reported that in postsulfonation reaction, only one sulfonic acid group per repeat unit of bisphenol A based polymers could be introduced and the acid group location of the electrophilic substitution was restricted at the activated ring ortho to the ether linkage.[11,19] The degree of sulfonation (DS) was
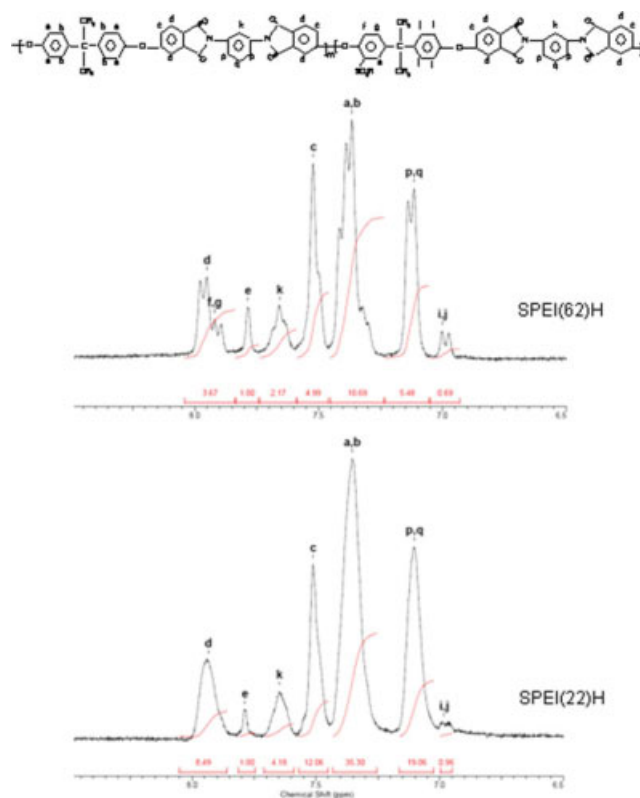

Figure 1 ^{1}H-NMR of SPEI sulfonated by TMSCS (numbers represent degree of sulfonation). [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]
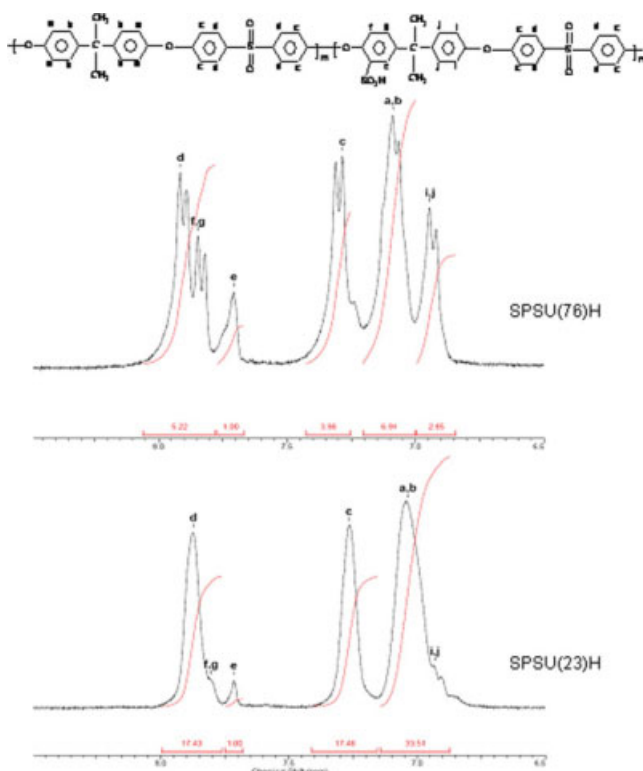
Figure 2 ^{1}H-NMR of SPSU sulfonated by TMSCS (numbers represent degree of sulfonation). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

quantified by ^{1}H-NMR in DMSO-d_6.[20] The analysis based on the chemical structure of the sulfonated PEI random copolymer is that there are 18 aromatic protons in the nonsulfonated repeat unit and 16 aromatic protons in the sulfonated repeat unit with one proton adjacent to sulfonic acid group at 7.79 ppm. Since the peak at 7.79 ppm is well resolved from all other peaks, it was used for quantification purpose. The degree of sulfonation is given by:

$$DS = \frac{18R}{1+2R}, \quad R = \frac{A_e}{A}$$

TABLE II
Peak Annotations and Chemical Shifts of Protons in SPAE-s

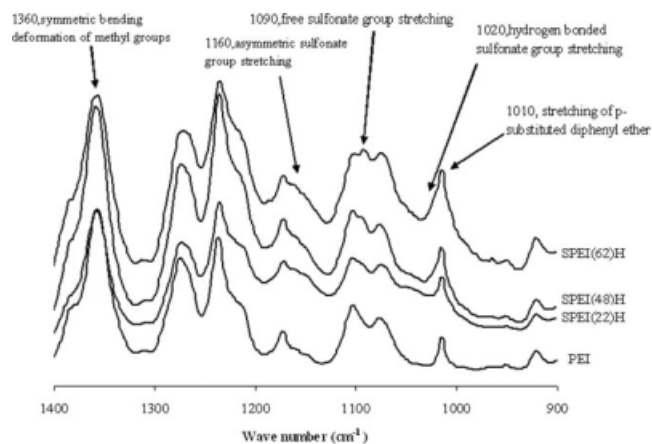| Positions	∂ (ppm)	
	SPEI	SPSU
a,b	7.1	7.08
c	7.35	7.31
d	7.93	7.91
e	7.79	7.71
f,g	7.88	7.84
i,j	6.98	6.94
k	7.64	–
p,q	7.51	–

Figure 3 FTIR spectra of SPEI sulfonated by TMSCS at various sulfonation levels (numbers refer to degree of sulfonation).

R is defined as the ratio of the area under the peak at 7.79 ppm, A_e, to the sum of the area under the peaks corresponding to all other aromatic protons, A. The sulfonation level of sulfonated PSU was determined by a similar method using the formula:

$$DS = \frac{16R}{1+2R}, \quad R = \frac{A_e}{A}$$

The degree of sulfonation and the corresponding ion exchange capacities are given in Table I.

FTIR

In sulfonated PEI, the absorption band at 1010 cm^{-1} was assigned to the symmetric stretching of the diphenylether unit along the polyarylene ether main chain and in plane ring vibration of para-substituted aryl ether. The absorption peak at 1360 cm^{-1},
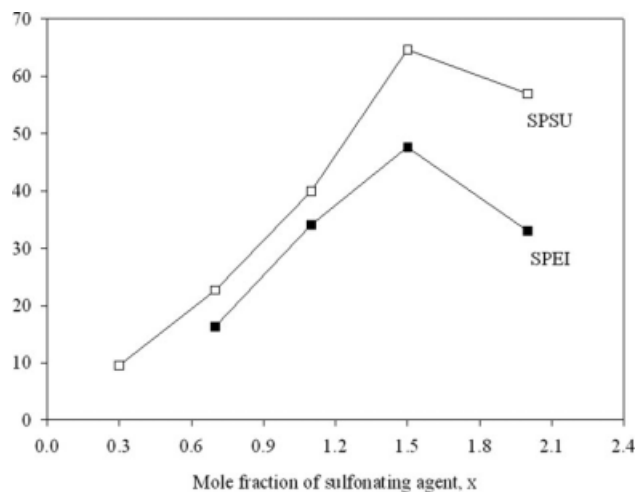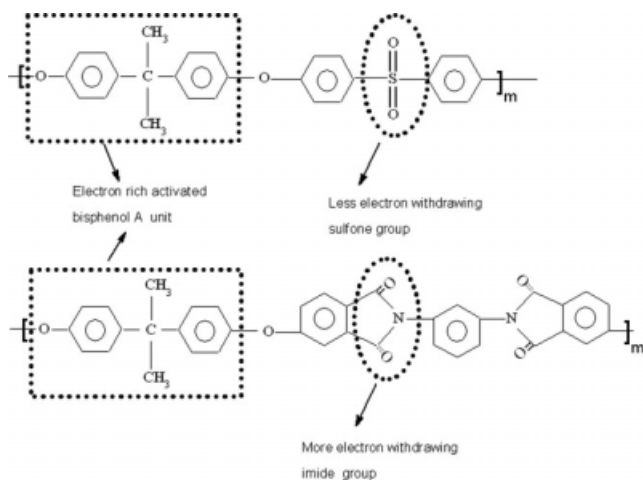

Figure 4 Degree of sulfonation of SPEI and SPSU as a function of TMSCS concentration.

Scheme 2 Effect of chemical structure of poly(arylene ethers) on sulfonation.

attributed to symmetric bending deformation of methyl groups in isopropylidene units is insensitive to the sulfonation. The bands at 1028, 1090, and 1160 cm^{-1} were assigned to the symmetric and asymmetric stretching of the sulfonate group. The type of counterion had significant influence on the sulfonate characteristic peaks- the symmetric stretching peak of sodium sulfonate at 1063 cm^{-1} in Nafion shifted to 1053 cm^{-1} in the acid form.[21,22] In this present study, in the acid form of sulfonated PEI, extensive hydrogen bond formation resulted broad absorption bands at 1020 and 1160 cm^{-1} due to symmetric and asymmetric stretching of sulfonic acid group with a relatively sharp peak at 1090 cm^{-1}, associated with free sulfonic acid groups shown in Figure 3. The spectral changes observed with increased sulfonation level are as follows: (i) intensity of the peak at 1090 cm^{-1} increased, (ii) the absorption bands at 1010
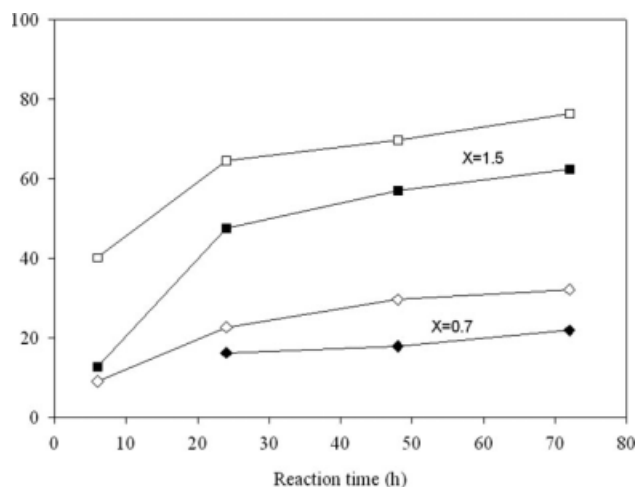

Figure 6 ^{1}H-NMR showing $\partial = 5.5$–6 ppm region of SPEI sulfonated by TMSCS and CSA.

and 1160 cm^{-1} gradually broadened, symmetric stretching band of sulfonate group overlapped with aryl ether peak.

Effect of poly(arylene ether) chemical structure on sulfonation

Figure 4 illustrates the effect of poly(arylene ether) (PAE) chemical structure on the degree of sulfonation. Comparison was made with similar TMSCS concentration, X, defined as the ratio of the number of moles of sulfonating agent to the number of moles of poly(arylene ether) repeat unit and the reactions were carried out at 30°C for 24 h. Two different bisphenol A based PAE-s were studied – PEI and PSU. The sulfonation level exhibits identical trends, at all X values, the level is higher in SPSU than in SPEI. The orientation of the sulfonic acid group in the activated aromatic ring was governed by the electron donating tendency of the ether oxygen. The variation in

Figure 5 Degree of sulfonation as a function of reaction time for two different concentration of TMSCS. The open and solid symbols represent SPSU and SPEI respectively.
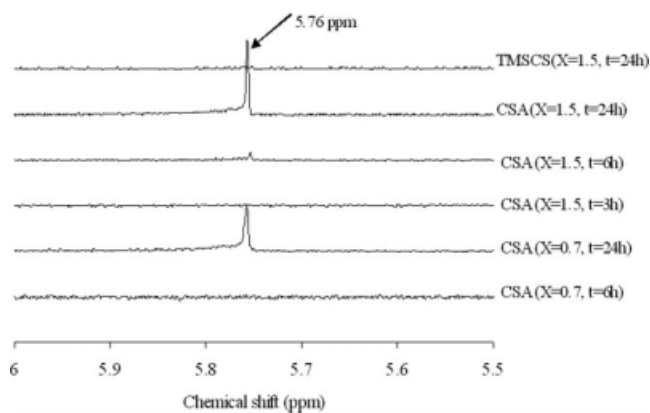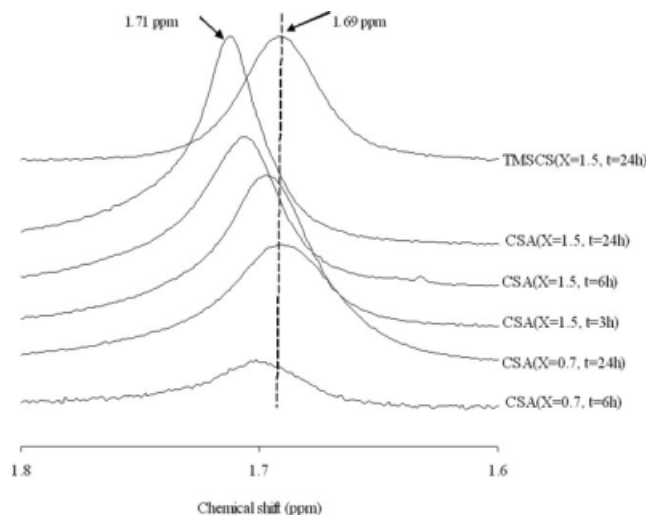

Figure 7 ^{1}H-NMR showing effect of two different sulfonating agents on the chemical shift position of isopropylidene unit.
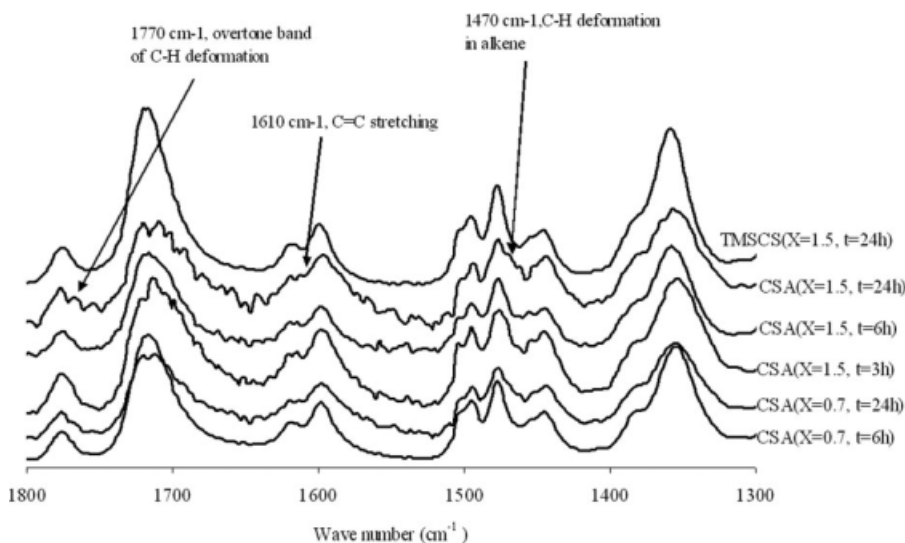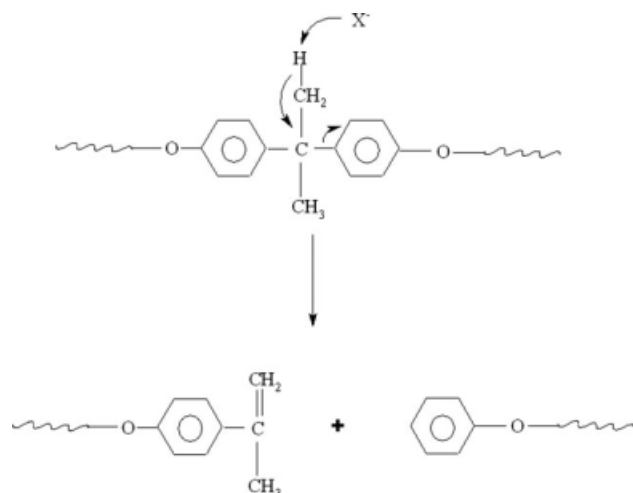
Figure 8 FTIR spectra of SPEI sulfonated by TMSCS and CSA.

reaction rates with PEI and PSU indicates that the different electron withdrawing groups in the deactivated units, as described in Scheme 2, also had influence on sulfonation although it occured at same bisphenol A unit of both poly(arylene ethers). Stronger electron withdrawing imide ring offered higher activation energy barrier to the approaching sulfonating agent through the more delocalization of electron cloud of the ether oxygen than the less electron withdrawing sulfone group and hence reduced the reaction rate. The higher ∂ values of protons in SPEI (shown in Table II) compared to that in SPSU further support this explanation.

Effect of reaction time and sulfonating agent concentration on sulfonation

The influence of reaction time on sulfonation of PAE-s was investigated by terminating the reactions after 6, 24, 48, and 72 h. The solutions were homogeneous even after 72 h. The sulfonation levels were accomplished with two different mole fraction of TMSCS, 0.7 and 1.5, shown in Figure 5. In all cases, initially the reaction rate was high and slowed down after 24 h. This was probably due to the electron withdrawing effect of the sulfonic acid group in the monosulfonated aromatic ring. With progress of the reaction, the increased sulfonic acid content caused enhanced deactivation of the aromatic rings, the decreased activated unit concentration drove the reaction towards steady state.

The changes in sulfonation level with variable TMSCS concentration, X is described in Figure 4. All the reactions were carried out at 30°C for 24 h. Similar trends are observed with both the PAE-s. The degree of sulfonation increases on increasing sulfonating agent concentration (mole fraction) up to 1.5, beyond this point it declines. This was possibly due to the degradation of PAE backbone. As discussed in the previous section, the initial high sulfonation
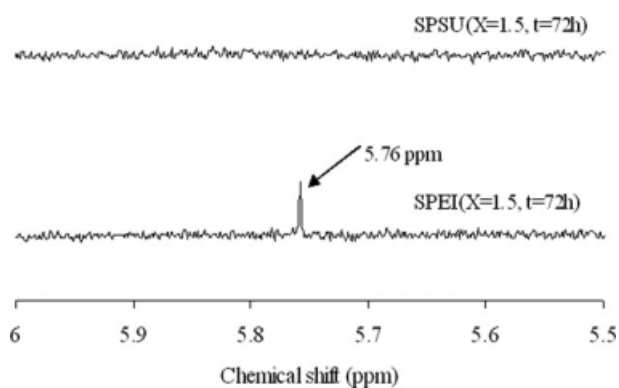

Scheme 3 Mechanism of acid catalyzed degradation of SPEI during sulfonation.

Figure 9 ^{1}H-NMR of SPEI and SPSU sulfonated by TMSCS in ∂ 5.5–6 ppm region after 72 h.

Figure 10 TGA thermograms of SPEI at different degrees of sulfonation.

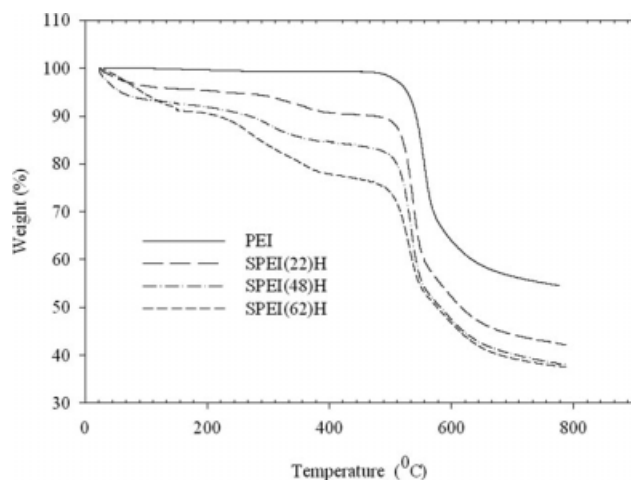**Figure 11** DSC thermograms of SPEI at different sulfonation levels.

rate caused generation of large amount of HCl. In presence of an acid, sulfonation and degradation were fairly competitive, thus reducing the efficiency of the sulfonating agent.

Comparison between two different sulfonating agents- TMSCS and CSA

The effect of two different sulfonating agents – CSA and its trimethylsilyl ester on sulfonation was systematically studied by analyzing sulfonated PEIs prepared under various conditions. The reaction medium was perfectly homogeneous with TMSCS while precipitation of the reaction product was observed immediately after the addition of CSA. Several evidences of structural modification were observed in ^{1}H-NMR and FTIR spectroscopic analysis (Figs. 6–8). ^{1}H-NMR spectra shows appearance of a new peak at 5.76 ppm in PEIs sulfonated by CSA, the intensity of which increases with the concentration of CSA and the reaction time, depicted in Figure 6. The chemical shift position at 1.69 ppm corresponding to methyl protons of isopropylidene unit

shifted to higher value upon sulfonation with CSA as compared to TMSCS under identical condition (Fig. 7). In FTIR spectra, a series of new absorption bands are clearly visible at 1770, 1610, 1470, and 840 cm^{-1} in SPEI when sulfonated with CSA, shown in Figure 8. PEI sulfonated using CSA under identical condition as TMSCS (i.e., $X = 1.5$, $t = 24$ h) showed significant reduction in solution viscosity.

The possible acid catalyzed degradation of PEI is illustrated in Scheme 3. Degradation was initiated through the attack of Cl$^-$ (released in the first step of sulfonation) at the methyl proton of isopropylidene unit and led to the generation of vinyl group. The peak at 5.76 ppm observed in ^{1}H-NMR (Fig. 6) can be attributed to these vinyl protons. FTIR analysis also reveals generation of vinyl group in the degradation products while sulfonation with CSA (Fig. 8), as evident from the following observations: (i) appearance of peak at 1610 cm^{-1} associated with conjugated C=C stretching, (ii) new peaks at 1770, 1470, and 840 cm^{-1} corresponding to C—H deformation of C=CH$_2$ were evident (band at 840 cm^{-1} not shown). In ^{1}H-NMR spectra (Fig. 9), it is seen that the peak at 5.76 ppm also appears with TMSCS after long reaction time, 72 h. Evidence of

TABLE III
Thermal Transitions and Degradation Temperatures of SPAE-s

Sample id.	T_g (°C)	Second step (200–400°C)		Third step (400–800 °C)		Residue (wt %)
		T_{max}	% wt loss	T_{max}	% wt loss	
PEI	220.6	–	–	555.7	45.5	54.5
SPEI(22)H	214.8	376.2	4.7	538.4	48.5	42.2
SPEI(48)H	203.7	300.3	7.3	534.4	46.7	38.1
SPEI(62)H	187.2	363.3	12.6	531.2	40.3	37.5
PSU	191.3	–	–	522.6	69.6	30.4
SPSU(23)H	195.8	318.9	17.4	519.9	57.4	22.4
SPSU(40)H	193.9	270.5	15.9	506.9	49.8	25.8
SPSU(76)H	139	318.1	24.8	513.4	46.4	21.2

TABLE IV
Inherent Viscosities and Tensile Properties of SPAE-s

| Sample id.	Tensile Strength (MPa)	Strain at Break (%)	Tensile Modulus (MPa)	η_i (dL/g)
PEI	75.2 ± 1.68	4.16 ± 0.45	2161.9 ± 247.13	0.14
SPEI(22)H	64.6 ± 0.01	3.85 ± 0.46	1912.1 ± 158.89	0.16
SPEI(48)H	30.5 ± 0.07	2.24 ± 0.69	1532.1 ± 137.24	0.2
SPEI(62)H	13.4 ± 1.29	1.92 ± 0.45	709.1 ± 152.71	0.47
PSU	77.6 ± 6.1	13.78 ± 2.61	2071.5 ± 122.33	0.11
SPSU(23)H	59.4 ± 2.73	11.22 ± 1.25	1970.3 ± 78.7	0.59
SPSU(40)H	53.3 ± 3.22	8.01 ± 2.27	1585.9 ± 219.27	0.63
SPSU(76)H	37.9 ± 2.84	6.41 ± 0.91	1385.1 ± 112.99	0.83
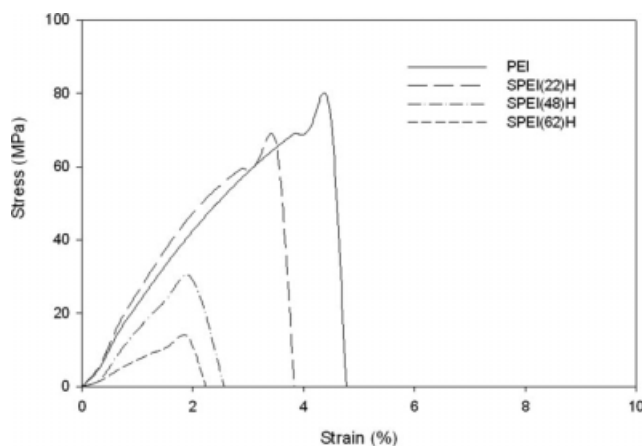
Figure 12 Stress–strain plots for SPEI at different degrees of sulfonation.

degradation in SPEI(62)H was also reflected from its lower viscosity than SPSU and this could account for the brittleness and the drastic loss of mechanical strength compared to other SPAE-s, and will be described in the following section. Thus the sulfonation and degradation were fairly competitive with CSA and occurred even at a lower acid concentration ($x = 0.7$). Sulfonation of PEI conducted with a higher concentration of TMSCS and/or prolonged reaction time also exhibited evidence of degradation at the isopropylidene unit initiated by HCl liberated during sulfonation. The degradation occurred through the same mechanistic path with the two different sulfonating agents.

Effect of sulfonation on thermal properties

TGA curves of SPAE exhibited three-step degradation pattern compared to one in unsulfonated PAE in nitrogen atmosphere, the curves for SPEI shown in Figure 10. The first step at ~100°C was due to the loss of water bonded to sulfonic acid groups. The second step between 200 and 400°C was attributed to the partial desulfonation; as reported by TGA-FTIR and TGA-mass spectrometry (MS) study.[23] The third step was related to the main chain decomposition. The temperature corresponding to the peak on derivative-weight (%) vs temperature, T_{max} and the corresponding weight loss of SPAE for the second and third step are described in Table III. The thermal stability was affected by the nature of the electron withdrawing groups (imide vs sulfone) in the deactivated moiety of SPAE. All SPAE-s exhibited thermal stability upto 500°C. T_{max} of second and third step were higher for SPEI than SPSU indicating better thermal stability of the sulfonated PEIs.

DSC results of SPAE-s in the acid form are compared with respect to PAE, as shown in Figure 11 for SPEI. The determination of T_g with accuracy was difficult due to the onset of desulfonation in the same temperature range. DSC thermograms of SPEI shows wide glass transition region. T_g decreases with increasing sulfonation level. Recently Bai et al. also reported a similar behavior in sulfonated poly(arylenethioethersulfone).[20]

According to the previous studies, the sulfonic acid groups in random sulfonated polymers associate to form ionic domains or clusters.[24–26] The evidence of cluster formation in random sulfonated polymers is the existence of two glass transition temperatures associated with the nonpolar matrix and the ionic cluster region and the ionic peak evident from small angle X-ray scattering (SAXS) studies which was attributed to the intermultiplet spacing in the cluster region. Several studies have addressed the factors influencing ion clustering- T_g of the parent polymer, ionic group content, nature of the ionic group, position of the ionic group relative to the polymer backbone, type of counter ion, steric constraints in the ion pair aggregation, amount and nature of the added low molecular weight compound (plasticizer). In this study, SAXS analysis of SPAE systems did not show any evidence of ion clustering even at high sulfonation level (not shown). Furthermore, single T_g was observed by DSC for all SPAE-s. This may be attributed to the restricted chain mobility due to the rigid polymer backbone (T_g of PEI is 220.6°C and T_g of PSU is 191.3°C) which offered hindrance to the phase separation. The results obtained in the study are in good agreement to the reported literature.[25,27] Two distinct morphological regions were found to exist in sulfonated polystyrene (T_g of the host polymer is 100°C) while in sulfonated poly(ether ether ketone) (T_g of the host polymer is 150°C), single phase behavior was evident.
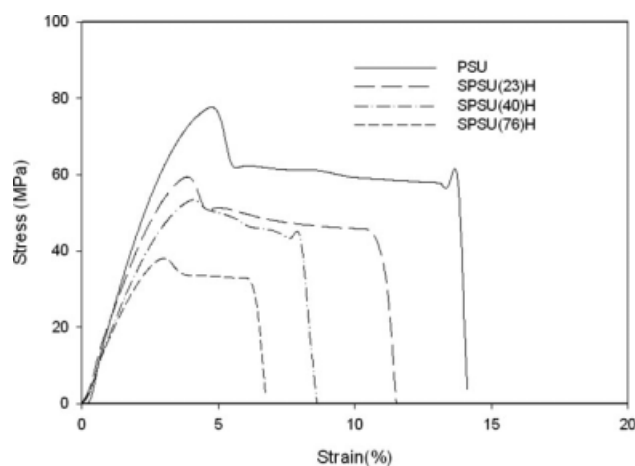

Figure 13 Stress–strain plots for SPSU at different degrees of sulfonation.

Effect of sulfonation on viscosity and mechanical properties

Table IV shows variation in inherent viscosity of SPAE-s with the degree of sulfonation. The viscosity increased with sulfonation level and the values of SPSU-s are to some extent larger than those of SPEI. Figures 12 and 13 compare tensile stress–strain properties of unmodified poly(arylene ethers) with the corresponding sulfonated ones, the results are also shown in Table for the ease of comparison. The tensile strength, modulus and elongation at break in all SPAE are lower as compared to the virgin polymers and the values progressively reduce with increasing degree of sulfonation. A significant decrease in the tensile parameters in SPEI(62)H was due to the PEI chain scission at the isopropylidene unit as evident from the viscosity measurement and spectroscopic analysis described in the previous section.

CONCLUSIONS

Two different bisphenol A based poly(arylene ethers)- PEI and PSU were sulfonated to various degrees by a controlled postsulfonation route using TMSCS. The introduction of sulfonic acid group was confirmed by ^{1}H-NMR and FTIR spectroscopy. The sulfonation method resulted random incorporation of sulfonic acid group at the activated bisphenol A unit of PAE. The optimum sulfonation level was obtained with 1.5 mole fraction of the sulfonating agent at 30°C. The stronger electron withdrawing imide ring reduced the sulfonation reaction rate of PEI compared to PSU. The sulfonation occurred at a faster rate initially, the rate decreased markedly beyond 24 h. The effects of degree of sulfonation on thermal and mechanical properties of SPAE-s were also studied. Degradation was evident during sulfonation at a higher TMSCS concentration and/or prolonged reaction time. It occurred at a faster rate while sulfonation with CSA than its silyl ester. The degradation followed the same mechanistic pathway with the two different sulfonating agents.

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