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Synthesis and Characterization of Sulfonated Polyimide Polymer Electrolyte Membranes

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Abstract: Several copolyimides have been synthesized with different combinations of comonomers in order to study the relationship between conductivity and water insolubility. *m*-Phenylenediamine (*m*-PDA), an angled comonomer, was introduced into the polymer backbone to increase water absorption, and resulted in higher proton conductivity. 2,2-bis(trifluoromethyl)benzidine (TFMB) was used as the comonomer to promote water insolubility. There is a good correlation between the water uptake and conductivity of the polyimides. The copolyimides that had high water uptake also generated high proton conductivity. Those polyimides had good mechanical properties. The copolyimides that have 27 mol% of TFMB and 9 mol% of *m*-PDA have reasonable conductivities and are insoluble in water at 90 °C, even though they have lower conductivities than those of the homopolymer.

Keywords: sulfonic acid, polyimides, *m*-phenylenediamine, 2,2-bis(trifluoromethyl)benzidine, proton conductivity, water insolubility.

Introduction

One of the most promising applications for sulfonated polymers is as proton conductive polymer electrolyte membranes (PEMs) in fuel cells.[1] A good example is perfluorosulfonated polymer such as Nafion® from Du Pont.[2-4] Even though much significant progress has been achieved using the perfluorosulfonated polymer, it still has problems.[5,6] The performance above 80 °C at atmospheric pressure is not good because it dries out and has poor conductivity at low humidity. The membrane has high methanol permeability. Also it is very expensive.

Mercier and co-worker[7] synthesized sulfonated polyimides for fuel cell membranes. However, their conductivity was not good compared to that of Nafion®. Litt *et al.* also developed a series of sulfonated copolyimides.[8] They were rigid rod linear polymers containing an angled or bulky comonomer that generated free volume lined with sulfonic acid groups. Such free volume absorbs water strongly even at relatively low humidity, resulting in higher proton conductivities at all humidity ranges than the polyimides from Merciers group or Nafion®. Also, the average chain distance between the polyimide backbones was measured by x-ray.[9] It showed that the copolymers had greater chain separations than the homopolymer. There was good correlation between x-ray spacing and conductivity of the polyimides. However, those copolyimides tended to dissolve or to be fragmented easily in water at elevated temperatures.

In the present work, 2,2'-bis(trifluoromethyl)benzidine (TFMB) was used as a comonomer to promote water insolubility. Hydrophobic CF_3 groups on benzidine tended to make the copolymer insoluble in water. Though the water insolubility of the polymer improved, the introduction of TFMB caused a significant loss of proton conductivity. Therefore, *m*-phenylenediamine (*m*-PDA), an angled comonomer, was introduced into the polymer to increase proton conductivity. The copolymer is angled; this forces the parallel liquid crystalline chains to separate and create free volume between the polymer backbones. Several copolyimides with different

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combinations of TFMB and *m*-PDA were synthesized in order to find new materials that have good conductivity and water insolubility.

Experimental

Materials. 4,4-Diamino-2,2-biphenyldisulfonic acid (DAPS) (TCI, 80%) was dispersed in water at 75 °C. Triethylamine (Aldrich, 99.5%) was added to the dispersion to get a homogeneous solution. After decolorizing with activated carbon, it was filtered over Celite. Conc. HCl (Fisher) was added to the solution until colorless crystals formed. It remained overnight. The precipitate was collected by filtration and dried under vacuum at 80 °C for 48 h. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (Aldrich) was purified by vacuum sublimation (290 °C, 0.5 mmHg). *m*-Cresol (Aldrich, 97%) was distilled under reduced pressure (80 °C, 5 mmHg). Triethylamine (Aldrich, 99.5%) was distilled from CaH_2. 2,2'-Bis(trifluoromethyl)benzidine (TFMB) (TCI, 98%) was recrystallized from methanol. *m*-Phenylenediamine (*m*-PDA) (Aldrich, 99%) was recrystallized from benzene. Benzoic acid (Aldrich 99.5%), 1,8-naphthalic anhydride (Aldrich) and methanol (Fisher) were used as received.

Syntheses of Model Compounds and Polymers.

Synthesis of Model Compound 1: DAPS (0.50 g, 1.45 mmol), triethylamine (0.33 g, 3.30 mmol) and *m*-cresol (20 mL) were placed in a 100 mL three neck round bottom flask equipped with a thermometer, a condenser and N_2 inlet/outlet. The dispersion was stirred at 140 °C for 0.5 h under N_2 to get a homogeneous solution. 1,8-Naphthalic anhydride (0.67 g, 3.34 mmol) was added to the solution. It was stirred at 200 °C for 15 h under N_2. After cooling to room temperature, the solution was poured into a mixture of concentrated HCl (200 mL) and methanol (500 mL) to get a yellow precipitate that was washed with methanol several times and dried under vacuum at 80 °C for 48 h to give 1.15 g (93%) of 1. ^{1}H-NMR (DMSO-d_6) δ 8.62-8.50 (m, 8H, Ar*H*, *p* and *o* position to carbonyl), 7.96 (t, 4H, Ar*H*, *m* position to carbonyl, J = 6.0 Hz), 7.94 (s, 2H, Ar*H*, *o* position to SO_3H), 7.72 (d, 2H, Ar*H*, *m* position to SO_3H, J = 8.2 Hz), 7.38 (dd, 2H, Ar*H*, *p* position to SO_3H, J_3 = 8.2 Hz, J_4 = 2.2 Hz); ^{13}C-NMR (DMSO-d_6) δ 164.3, 144.7, 138.1, 135.0, 134.7, 133.6, 132.0, 131.4, 129.1, 128.6, 127.8, 123.3; IR (KBr) cm^{-1} 1708 and 1663 (C=O), 1193 (S=O). Elem. Anal. Calcd. for $C_{36}H_{20}N_2O_{10}S_2(6.5H_2O)$: C, 52.60%; H, 4.01%; N, 3.41%. Found: C, 52.10%; H, 3.42%; N, 3.31%.

Synthesis of Model Compound 2: In a 250 mL three neck three neck flask equipped with a thermometer, a condenser and N_2 inlet/outlet, *m*-PDA (2.02 g, 18.84 mmol) and *m*-cresol (70 mL) were placed. It was heated to 170 °C and NTDA (0.25 g, 0.93 mmol) was added portion-wise for 1 h under N_2 atmosphere. It was stirred at 200 °C for 15 h. After the reaction mixture cooled to room temperature, it was poured into methanol (600 mL) and a gray material precipitated. It was washed with methanol several times and dried under vacuum at 50 °C for 24 h to give 0.39 g (93%) of **2**. ^{1}H-NMR (DMSO-d_6) δ 8.71 (s, 4H, Ar*H*, naphthyl group), 7.18 (t, 2H, Ar*H*, *m* to NH_2, J = 7.9 Hz), 6.70-6.50 (m, 6H, Ar*H*, *p* and *o* position to NH_2), 5.32 (s. 4H, N*H*$_2$); ^{13}C-NMR (DMSO-d_6) δ 163.3, 150.0, 136.7, 130.9, 129.7, 127.5, 127.1, 116.4, 114.7, 114.4; IR (KBr) cm^{-1} 3438 and 3363 (N-H$_2$), 1711 and 1673 (C=O). Elem. Anal. Calcd. for $C_{26}H_{16}N_4O_4$: C, 69.64%; H, 3.57%; N, 12.50%. Found: C, 69.43%; H, 3.80%; N, 12.39%.

Synthesis of Homopolymer. DAPS (1.30 g, 3.77 mmol), triethylamine (0.95 g, 9.39 mmol) and *m*-cresol (45 mL) were placed in a 100 mL three neck round bottom flask equipped with a thermometer, a condenser and N_2 inlet/outlet. The dispersion was stirred at 140 °C for 0.5 h under N_2 to get a homogeneous solution. NTDA (1.01 g, 3.77 mmol) and benzoic acid (0.94 g, 7.70 mmol) were added to the solution. It was stirred at 200 °C for 24 h under N_2. After cooling to room temperature, the solution was poured into a mixture of concentrated HCl (200 mL) and methanol (500 mL) to get thin red fibers. These fibers were collected and dried under vacuum at room temperature for 24 h. The polymer was dissolved in DMSO (125 mL) and the solution was poured into a mixture of concentrated HCl (200 mL) and methanol (500 mL) to get a yellow precipitate; the suspension was stirred for 24 h. This process was repeated until the ^{1}H-NMR of the precipitate showed no triethylammonium resonances. The polymer was extracted with methanol in a Soxhlet extractor for 24 h to remove excess HCl. It was dried under vacuum at 80 °C for 35 h to give 2.13 g. ^{1}H-NMR (DMSO-d_6) δ 8.78 (bs, 4H, Ar*H*, naphthyl group), 7.79 (bs, 2H, Ar*H*, *m* position to SO_3H), 7.41 (bs, 2H, Ar*H*, *p* position to SO_3H); IR (KBr) cm^{-1} 1712 and 1673 (C=O), 1203 (S=O).

Synthesis of Random Copolymers. A typical synthetic procedure for the random copolymers is as follows, exemplified for **RmP10** (random copolyimide which has 10 mole% of *m*-PDA). DAPS (0.75 g, 2.18 mmol), *m*-PDA (0.026 g, 0.24 mmol), triethylamine (0.66 g, 6.60 mmol) and *m*-cresol (29 mL) were placed in a 100 mL three neck round bottom flask equipped with a thermometer, a condenser and N_2 inlet/outlet. The dispersion was stirred at 140 °C for 0.5 h under N_2 to get a homogeneous solution. NTDA (0.65 g, 2.42 mmol) and benzoic acid (0.59 g, 4.84 mmol) were added to the solution. It was stirred at 200 °C for 24 h under N_2. After cooling to room temperature, the solution was poured into a mixture of concentrated HCl (200 mL) and methanol (500 mL) to get thin red fibers. These fibers were collected and dried under vacuum at room temperature for 24 h. The polymer was dissolved in DMSO (100 mL) and the solution was poured into a mixture of concentrated HCl (200 mL) and methanol (500 mL) to get a yellow precipitate; the suspension was stirred for 24 h. This process was repeated until the ^{1}H-NMR of the precipitate showed no triethylammonium resonances. The polymer was extracted with meth-

anol in a Soxhlet extractor for 24 h to remove excess HCl. It was dried under vacuum at 80 °C for 35 h to give 1.34 g. IR (KBr) cm^{-1} 1713 and 1675 (C=O), 1200 (S=O).

Synthesis of Block Copolymers. A typical synthetic procedure for block copolymers is as follow, exemplified for **BTFMB27mP9[7/(3+1)]** (block copolyimide which has 27 mole% of TFMB and 9 mole% of *m*-PDA). DAPS (0.68 g, 1.97 mmol), triethylamine (0.52 g, 5.1 mmol) and *m*-cresol (37 mL) were placed in a 100 mL three neck round bottom flask equipped with a thermometer, a condenser and N_2 inlet/outlet. The dispersion was stirred at 140 °C for 0.5 h under N_2 to get a homogeneous solution. NTDA (0.45 g, 1.69 mmol) and benzoic acid (0.76 g, 6.22 mmol) were added to the solution. It was stirred at 200 °C for 10 h under N_2. More NTDA (0.15 g, 0.56 mmol) was added and the solution was heated for 0.5 h. Then, NTDA (0.23 g, 0.84 mmol), TFMB (0.27 g, 0.84 mmol) and *m*-PDA (0.03 g, 0.28 mmol) were added and stirred at 200 °C for 12 h under N_2. After cooling to room temperature, the solution was poured into a mixture of concentrated HCl (200 mL) and methanol (500 mL) to get thin red fibers. These fibers were collected and dried under vacuum at room temperature for 24 h. The polymer was dissolved in DMSO (100 mL) and the solution was poured into a mixture of concentrated HCl (200 mL) and methanol (500 mL) to get a yellow precipitate; the suspension was stirred for 24 h. This process was repeated until the ^{1}H-NMR of the precipitate showed no triethylammonium resonances. The polymer was extracted with methanol in a Soxhlet extractor for 24 h to remove excess HCl. It was dried under vacuum at 80 °C for 35 h to give 1.62 g. IR (KBr) cm^{-1} 1714 and 1677 (C=O), 1199 (S=O), 1314 (C-F).

Fabrication of Polyimide Films. 1.5 g of the polymer (free acid form) was dissolved in 30 mL of DMSO at room temperature. The viscous polymer solution was poured on a glass plate. The thickness of the solution on the glass was controlled using an adjustable doctor blade. It was placed in an oven equipped with a thermometer, and DMSO was removed under reduced pressure (0.1 mmHg) at room temperature for 30 min. Oven temperature increased to 80 °C over 30 min under the same pressure. Residual DMSO was removed by heating it under vacuum at 80 °C for 30 h. The film was detached from the glass plate and soaked in methanol for 24 h to remove traces of DMSO in the film. It was then dried under vacuum at room temperature.

Techniques. ^{1}H-NMR (200 MHz) and ^{13}C-NMR (50 MHz) spectra were recorded on a Varian Gemini 200 spectrometer at 19 °C in DMSO-d_6 with tetramethylsilane (TMS) internal standard. A diluted DMSO solution of model compound (powder form) or polyimide (membrane) was cast on a KBr plate and dried under vacuum (0.1 mmHg) at 80 °C for 30 h. Fourier transform infared (FT-IR) spectra were obtained on a Bomem Michelson MB110 FT-IR spectrophotometer that was equipped with a liquid nitrogen cooled, mercury-cadmium-telluride (MCT) detector. TGA was carried out on a TA instruments TGA 2950, under 90 mL/min of N_2 flow rate and 20 °C/min of heating rate. Also, FT-IR (Bio-Rad FTS 60A) with a gas phase cell with a dry air stream was used for analysis of gases evolved during the degradation of the specimen. The FT-IR was interfaced with the TGA through a heated glass pipeline. Both the line and evolved gases were heated at 260 °C. FT-IR spectra of the gases were collected at a spectral resolution of 8 cm^{-1} and at a time resolution of 1 second.

Proton conductivity was measured at room temperature using a 4-point probe configuration[10] Solartron apparatus in the AC mode at different relative humidities.[11] The applied frequency was from 10^5 to 1 Hz. Two outer probes supply current to the cell, while two inner electrodes measure the potential drop. The resistance was measured twice by switching the sequence of the probes and the values were averaged.

An Instron (model no. 5565) was used to measure the stress/strain properties of the polyimide films. They were tested under ambient conditions at 10 mm/min of crosshead speed. Film specimens were prepared according to Standard Test Method for Tensile Properties of Plastics (ASTM).[12]

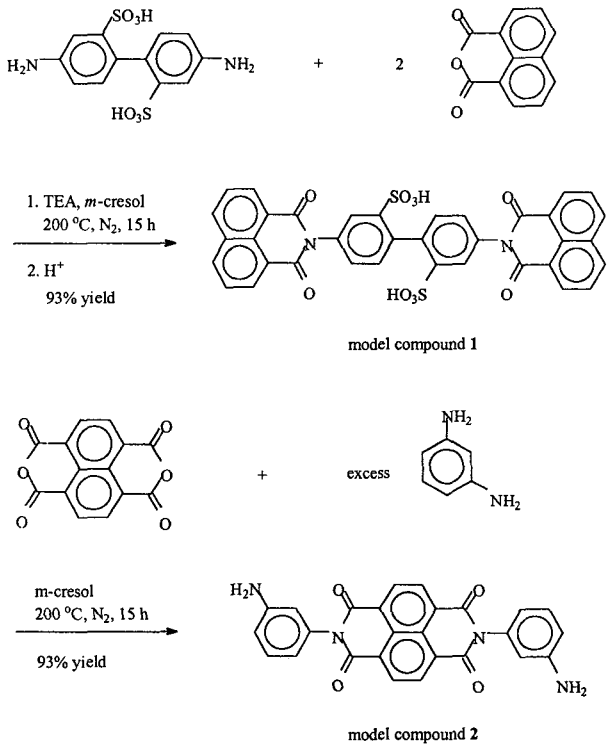
Water uptake of polymers was measured as follows. Polymer films were placed in weighing bottles and dried under vacuum (0.1 mmHg) at 80 °C for 36 h. After weighing, the films and weighing bottles were placed for 24 h in a desiccator containing $LiCl/H_2O$ solutions at a given relative humidity and reweighed.

Water insolubility of polymers was measured as follows. Several small pieces of polymer film (0.5 cm × 0.5 cm) were placed in 90 °C DI water in a round bottom flask equipped with a condenser and a thermometer. The change of the film shape was observed.

Results and Discussion

Synthesis of Model Compounds. Model compound **1** was synthesized by a one-step method from the reaction of 4,4'-diamino-2,2'-biphenyldisulfonic acid (DAPS) with 1,8-naphthalic anhydride in *m*-cresol. Model compound **2** was obtained by the reaction of a large excess of *m*-PDA with 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA). Their synthetic routes are shown in Scheme I. Their structures were confirmed by ^{1}H-NMR, ^{13}C-NMR and IR. Figures 1 gives the ^{13}C-NMR spectrum for **1**. Assignments of peaks for the compound are given in the Figure. The ^{13}C-NMR peak for the carbon 5 might be buried under the peaks for the carbon 2, 9 and 12.

There has been some discussion in the literatures about the formation of isoimide.[13] Isoimides can be readily formed from the reaction of six-membered dicarboxylic anhydrides with amines, because the six-membered isoimide ring is relatively stable. Therefore, analysis of the model compound is very important to determine the structure of the six-mem-



Scheme I. Synthesis of model compounds.

bered imide ring. One of the most significant features for cyclic imidization of the model compound is the ^{13}C-NMR peak for the imide group carbons at 164.3 ppm. If isoimides were formed, two peaks would appear for the C=O and C=N carbons. Also, high yields (93%) of the model compounds containing only one ^{13}C carbonyl peak were obtained.

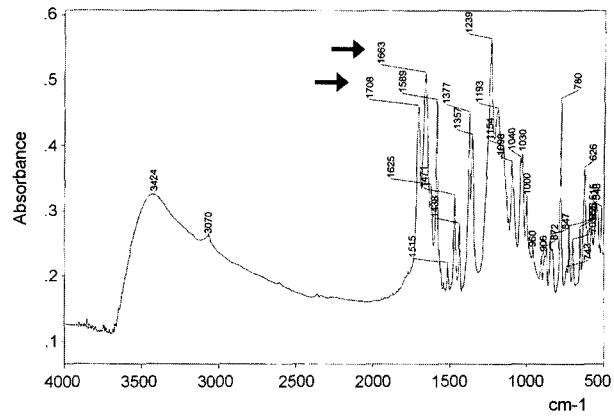


Figure 2. FT-IR spectrum of model compound **1**.

This confirms the quantitative formation of the imide rings.

The FT-IR spectrum of **1** is shown in Figure 2. Characteristic absorption bands for the imide group appear at 1708 (asymmetric C=O stretching) and 1663 (symmetric C=O stretching) cm^{-1}, respectively. Usually, five-membered imide rings show characteristic absorption bands for the imide group around 1780 (asymmetric C=O stretching) and 1720 (symmetric C=O stretching) cm^{-1}. The FT-IR spectrum of **2** showed the characteristic absorption bands for the imide group at 1711 (asymmetric C=O stretching) and 1673 (symmetric C=O stretching) cm^{-1}. The characteristic absorption bands for NH_2 at 3438 (asymmetric N-H stretching) and 3363 (symmetric N-H stretching) cm^{-1} indicate the existence of primary amines. The FT-IR analysis of the model compounds was used for the structural identification of polymers.

Synthesis of Polymers. The acronym definition for copolymers is presented in Figure 3. Table I shows the molar ratio

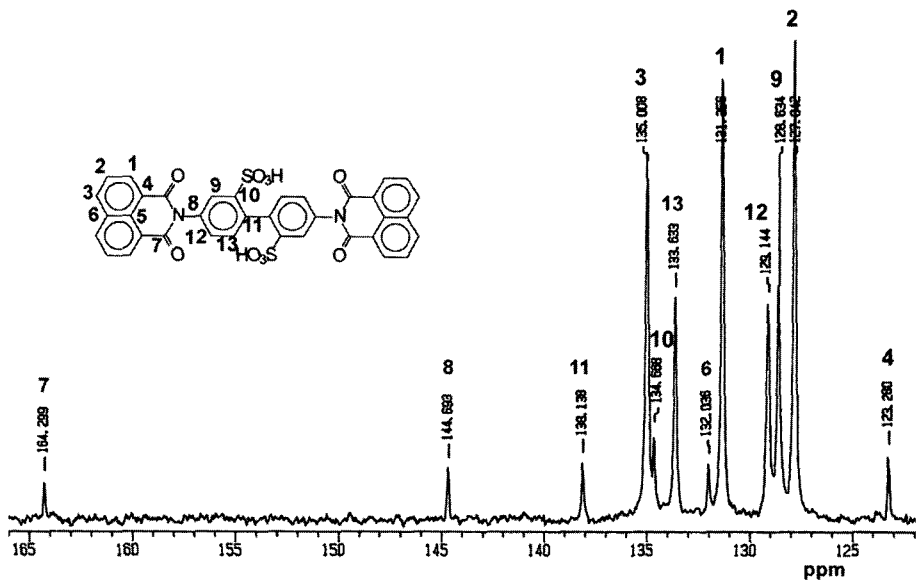


Figure 1. ^{13}C-NMR spectrum of model compound **1** in DMSO-d_6.

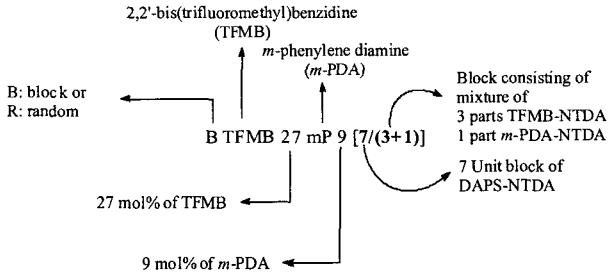
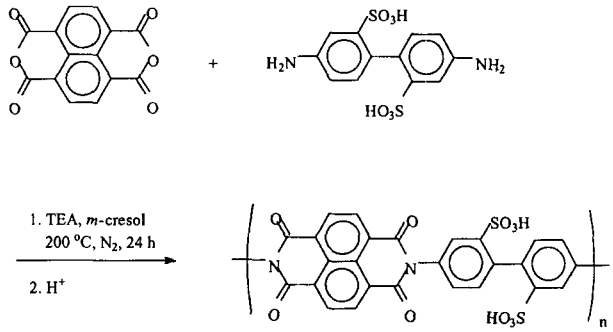


Figure 3. Acronym definition for copolymers.

Table I. Nomenclature for Copolymers

Polyimides	Mole% of Comonomers		
	DAPS	*m*-PDA	TFMB
Homopolymer	100		
RmP10	90	10	
BTFMB18mP9[8(2+1)]	73	9	18
BTFMB27mP9[7(3+1)]	64	9	27
RTFMB27mP9	64	9	27
RTFMB10	90		10
BTFMB30[7/3]	70		30
RTFMB33	67		33
BTFMB36[7/4]	64		36
RTFMB50	50		50

DAPS: 4,4'-diamino-2,2'-biphenyldisulfonic acid.
m-PDA: *m*-phenylenediamine.
TFMB: 2,2'-bis(trifluoromethyl)benzidine.



Scheme II. Synthesis of homopolymer.

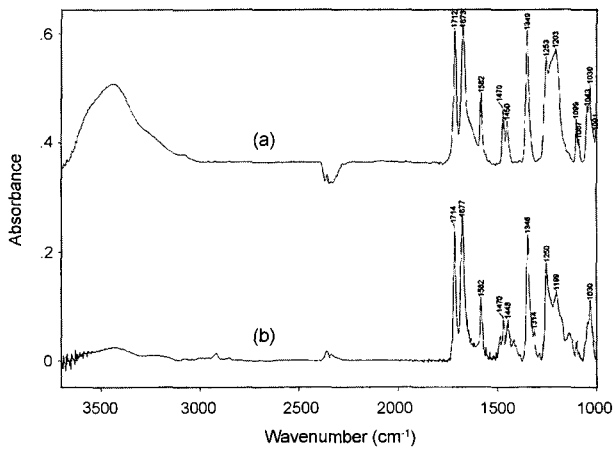
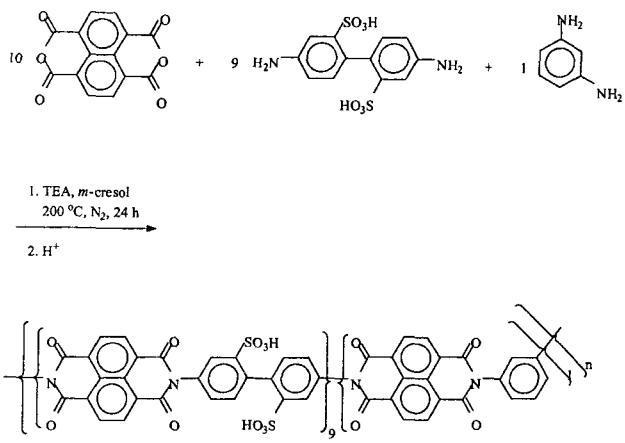


Figure 4. FT-IR spectra of homopolymer (a) and BTFMB27mP9 [7/(3+1)] (b).

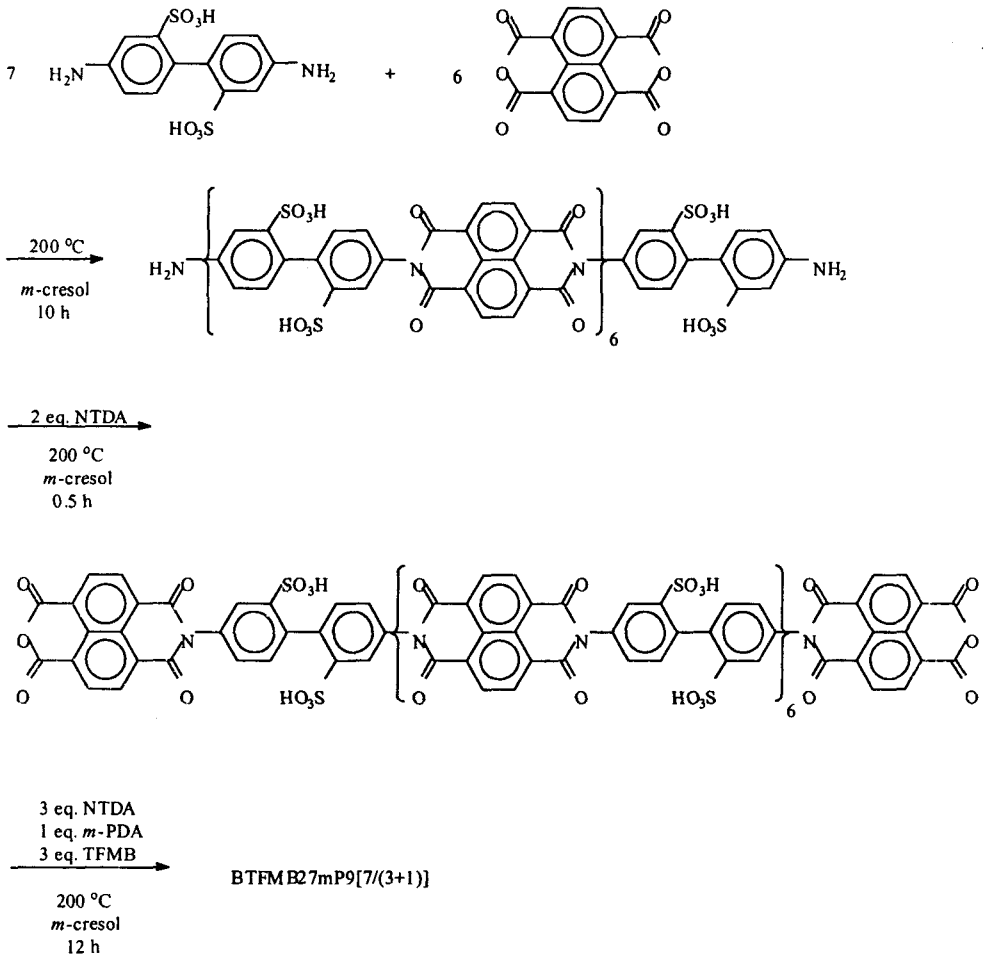
of diamine monomers in the polyimides. Homopolyimide was synthesized by the method used for the model compounds (Scheme II). The FT-IR spectrum of the homopolymer is shown in Figure 4(a). Asymmetric C=O stretching and symmetric C=O stretching absorption bands appear at 1712 and 1673 cm^{-1}. Random copolyimides were synthesized by the method used for the homopolyimide. A typical synthetic scheme is presented in Scheme III. Block copolymers were prepared using similar method (Scheme IV). The FT-IR spectrum of one of the block copolymers is shown in Figure 4(b) (BTFMB27mP[7/(3+1)]). The characteristic absorption peaks for asymmetric C=O stretching and symmetric C=O stretching appear at 1714 and 1677 cm^{-1}.

Thermal Analysis. A homopolymer film was dried at 80 °C under vacuum (0.1 mmHg) for 30 h, and it was placed immediately in TGA device and tested. The TGA result is presented in Figure 5(a). The polymer contained one water molecule per sulfonic acid group, which corresponds to the 6% weight loss. Another homopolymer film was equilibrated at ambient conditions (at 20 °C and 30% relative humidity) for 1 day after drying (at 80 °C under vacuum (0.1



Scheme III. Synthesis of RmP10.

mmHg) for 30 h) and then tested. The TGA result is presented in Figure 5(b). The polymer had three water molecules per sulfonic acid, calculated from its 18% weight loss. Even



Scheme IV. Synthesis of BTFM27mP9[7/(3+1)].

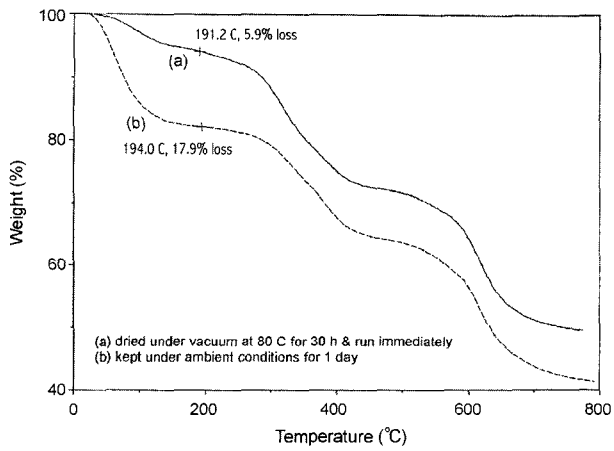


Figure 5. TGA of homopolymer.

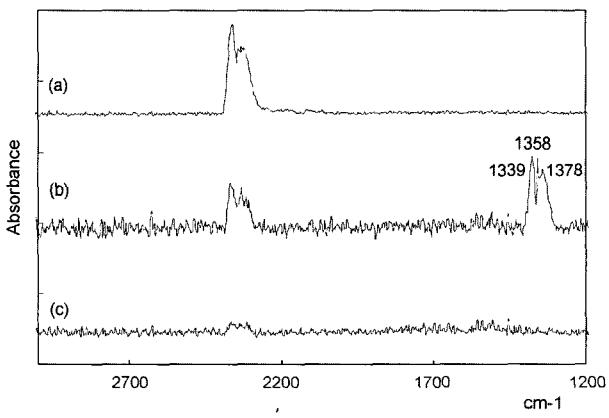


Figure 6. FT-IR spectra of gases from degraded homopolymer at 50-200 °C (a), 270-410 °C (b), and 460-700 °C (c).

though the polymer was dried under vacuum for a very long time (90 h) at 95 °C, the water content of the polymer film could not be reduced further. Also, the water content did not change after a week under ambient conditions.

Evolved gases from the degrading polymer during the TGA measurement were scanned using FT-IR. The spectra are shown in Figure 6. At 270-410 °C, multiple peaks (1339, 1358 and 1378 cm^{-1}) were observed. The peak positions and

shapes are similar to those of the spectrum of SO_2 (from the Aldrich handbook[14]). So, we conclude that SO_2 is evolved during the decomposition at 270-410 °C.

Proton Conductivity. Table II shows the conductivities of polyimides. The conductivity of RmP10, which has an angled comonomer was higher than that of the homopolymer at low humidity. As the mole ratio of TFMB in the copolymers increased, the conductivities decreased.

BTFMB27mP9[7/(3+1)] and RTFMB27mP9, with the same molar ratio of comonomers (see Table I), showed similar conductivities. They had same molar ratio of sulfonated to non-sulfonated units (64% *vs* 36%) as BTFMB36[7/4] which had no *m*-PDA unit in it. However, they had higher conductivities at all humidities than the linear copolymer, BTFMB36[7/4]. In our previous report,[8] the copolyimides contained an angled or bulky comonomer that generated free volume lined with sulfonic acid groups. It absorbs water strongly even at relatively low humidity, resulting in higher proton conductivities over the whole humidity range than the homopolyimide. Also, in another study, the average chain distance between the polyimide backbones was measured by x-ray.[9] It showed that the copolymers had greater chain separations than the homopolymer. There was good correlation between x-ray spacing and conductivity of the polyimides. In this study, the introduction of an angled comonomer, *m*-PDA, into the polymer produced higher conductivities. Also, BTFMB27mP9[7/(3+1)]and RTFMB27mP9 are less hydrophobic than BTFMB36[7/4], because TFMB is more hydrophobic than *m*-PDA.

Water Uptake. Water retention capacity of polyimides was determined by water uptake measurement. Table III lists the water uptake data of polyimides at different relative

Table II. Conductivities of the Polyimides at 25 °C as a Function of Relative Humidity

Relative Humidity (%)	Conductivity (S/cm)				
	Homo-polymer	RmP10	BTFMB18mP9[8/(2+1)]	BTFMB27mP9[7/(3+1)]	RTFMB27mP9
100	0.23	0.21	0.11	0.11	0.11
75	0.038	0.040	0.015	0.019	0.018
50	9.3E-3	10E-3	3.6E-3	3.2E-3	4.2E-3
35	2.6E-3	3.8E-3	1.3E-3	1.3E-3	2.1E-3
15	2.9E-4	5.1E-4	1.1E-4	1.8E-4	1.2E-4

Relative Humidity (%)	Conductivity (S/cm)				
	RTFMB10	BTFMB30[7/3]	RTFMB33	BTFMB36[7/4]	RTFMB50
100	0.21	0.13	0.061	0.064	0.029
75	0.027	0.016	9.3E-3	9.3E-3	1.2E-3
50	8.0E-3	2.8E-3	2.8E-3	1.8E-3	1.1E-4
35	1.0E-3	1.0E-3	5.6E-4	2.9E-4	2.7E-6
15	1.1E-4	8.3E-5	1.3E-5	2.1E-5	

All films were cast in the acid form from DMSO.

Table III. Water Uptake of Homopolymer and Selected Copolyimides at 25 °C

Relative Humidity (%)	Weight of Water / 100 gm of Polymer (λ)				
	Homo-Polymer[a]	Homo-polymer[b]	RmP10[a]	BTFMB27mP9[7/(3+1)][a]	BTFMB36[7/4][a]
90	54.8 (8.8)		54.0 (9.3)	39.5 (9.5)	36.4 (9.0)
75	33.7 (5.4)	36.8 (6.0)	35.2 (6.0)	26.1 (6.2)	22.4 (5.5)
50	24.3 (3.9)	30.2 (4.8)	25.2 (4.3)	18.2 (4.4)	15.9 (3.9)
35	19.0 (3.0)	21.3 (3.4)	20.2 (3.5)	14.4 (3.4)	11.8 (2.9)
15	12.8 (2.1)	15.5 (2.5)	14.1 (2.4)	9.7 (2.3)	7.6 (1.9)

λ = water molecules per sulfonic acid groups.

[a]Films were cast in the acid form from DMSO; samples were dried under vacuum (0.1 mmHg) at 80 °C for 36 h.

[b]Films were cast as the triethylamine salt from *m*-cresol, and then acidified; samples were dried under vacuum (0.3 mmHg) at 80 °C for 72 h (Yue Zhangs PhD thesis).[13]

humidities. The incorporation of *m*-PDA in copolyimides produced higher water uptake than corresponding linear polyimides. There was good correlation between water uptake and conductivity of the polyimides.

The water uptake data for homopolymer in this paper are different from those in Yue Zhangs PhD thesis.[15] Previously, the polymer film was cast as the triethylamine salt form from *m*-cresol, and then acidified. So, it had physically loose structure and higher water uptake.

Mechanical Properties. The mechanical properties of polyimides are presented in Table IV. The polyimide films had moduli ranging between 1.30 and 2.10 GPa. When *m*-PDA was introduced into the polymer, elongation increased. When TFMB was the only comonomer, the modulus of the copolymer was much higher than that of the homopolymer and elongation was lower, e.g. RTFMB30.

Water Solubility. Water solubility of the polyimides was tested in 90 °C DI water. The results are summarized with the conductivities at 50% relative humidity in Table V. As the mole ratio of TFMB in the copolymer increased, the polymers were less affected by the water treatment, but their conductivities decreased. Films of BTFMB27mP9[7/(3+1)] and RTFMB27mP9 which have 64% sulfonated unit were unchanged in DI water at 90 °C. If the molar ratio of the sulfonated unit is over 64%, the polymer is dissolved in DI water at 90 °C.

Conclusions

Model compounds were synthesized by a one-step reaction in *m*-cresol with high yield. ^{13}C-NMR analyses of the compounds confirmed the formation of the imide ring. Homo-polyimide and copolyimides were synthesized using the same method as for the model compounds. We found that SO_2 was evolved at 270-410 °C range from the degradation of the homopolymer. Copolyimides with different combinations of 2,2'-bis(trifluoromethyl)benzidine (TFMB) and *m*-phenylenediamine (*m*-PDA) were synthesized in order to find materials with good conductivity plus water insolubility. As the mole ratio of TFMB in the copolymer increased, the conductivities decreased and the water insolubility improved because of its hydrophobicity. The introduction of an angled comonomer, *m*-PDA, into the polymer increased the conductivities compared to corresponding linear polymers. Copolymers which have 27 mole% of TFMB and 9 mole% of *m*-PDA such as BTFMB27mP9[7/3+1] and RTFMB27mP9 had reasonable conductivity, and did not dissolve in water at 90 °C. These polymers had good mechanical properties.

Table IV. Mechanical Properties of Polyimide Films under Ambient Condition

Polymers	Young's modulus (GPa)	Stress at Break* σ_B (MPa)	Elongation at Break ε_B (%)
Homopolymer (III57)**	1.32 ± 0.02	71 ± 10	9 ± 1.5
Homopolymer (III60)**	1.49 ± 0.13	87 ± 18	9 ± 0.1
BTFMB30 [7/3]	2.10 ± 0.20	101 ± 13	6 ± 1.4
BTFMB18mP9 [8/(2+1)]	1.50 ± 0.02	140 ± 5	20 ± 0.5
BTFMB27mP9 [7/(3+1)] (III62)**	1.30 ± 0.10	84 ± 4	16 ± 1.0
BTFMB27mP9 [7/(3+1)] (III65)**	1.60 ± 0.09	120 ± 15	20 ± 0.5
RTFMB27mP9	1.50 ± 0.20	106 ± 15	12 ± 0.5

*Samples does not show yield; stress at break is maximum stress. **Batch number.
All films were cast in the acid form from DMSO. Crosshead speed: 10 mm/min.
Size of rectangular test region on a dumb-bell specimen is 3 mm × 9.5 mm, width× length.

Table V. Water Solubility of Homopolymer and Copolymers

Polymers	Solubility (DI water at 90 °C)	Conductivity (S/cm) at 50% RH	Molar Ratio of Sulfonated Unit
Homopolymer	dissolves immediately	9.3E-3	100
RTFMB10	dissolves after 1 h	8.0E-3	90
BTFMB18mP9[8/(2+1)]	dissolves after 2 days	3.6E-3	73
BTFMB30[7/3]	dissolves after 1 day	2.8E-3	70
RTFMB27mP9	unchanged after 10 days	4.2E-3	64
BTFMB27mP9[7/(3+1)]	unchanged after 1 month	3.2E-3	64
RTFMB50	unchanged after 7 days	1.1E-4	50

All films were cast in the acid form from DMSO.

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