Synthesis and Properties of Ionic, Rigid-Rod, and Thermally Stable Polyimides Containing Bipyridinium Triflates

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ABSTRACT: A series of 4,4′-(1,4-phenylene)bis(*N*-amino-2,6-diphenylpyridiniumtriflate) compounds were synthesized by reaction of 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium triflate) with various aromatic diamines. They were used as starting materials for the preparation of novel ionic rigid-rod polyimides. The resulting poly(amic acid)s had inherent viscosities of 0.73−1.93 dL/g. Thermal cyclodehydration of poly(amic acid)s afforded the polyimides. Their inherent viscosities were in the range of 0.31−0.58 dL/g. These polyimides are basically amorphous and are soluble in polar aprotic solvents. A lyotropic behavior could be observed in a concentrated solution of dimethylformamide and methylpyrrolidone. Thermogravimetric analyses showed that they are thermally stable with 5% weight losses recorded in the range of 459−478 °C under nitrogen and 469−489 °C in air. The polyimides had a tensile strength range of 59−93 MPa, and an elongation at break range of 5−9%. Reversibe color development of these polyimides could be observed upon irradiation in solution or in a polymer matrix.

Introduction

Aromatic polyimides have been recognized as representative of the class of thermally stable polymers because of their high thermal and thermooxidative stability and excellent electrical and mechanical properties. They also display chemical and solvent resistance, good adhesive properties, light stability, and dimensional stability. With the unique combination of these properties, polyimides were widely used as high-temperature films, fibers, coatings, adhesives, and matrices for high performance composites.[1−5] However, applications of polyimides have been limited in many fields because they are normally insoluble in common organic solvents. The rigid structure which gives excellent mechanical properties is often accompanied by poor solubility. Improved solubility has been attained by the incorporation of flexible[6−8] or bent bridging linkages[9] into the polymer backbone and by the introduction of bulky substituents[10−12] along the polymer. In our previous work, we have introduced aromatic bipyridinium perchlorate into polyimide backbones via bipyridinium-based aromatic diamines.[13] Bipyridinum salts known as viologens can add two electrons stepwise with an obvious color change by chemical, electrochemical, or photochemical methods.[14−16] Polyimides containing a bipyridinium ion in the polymer backbone may be utilized as easily removable electron-transfer catalysts, ionic conductors, and ion-exchange membranes.[17] As we expected, these bipyridinium-based polyimides are soluble in several polar aprotic solvents such as DMF and DMAc. However, the thermal stability of the polymers that were obtained diminished, and they became too brittle to form tough films.

Our objective is the synthesis and characterization of a new series of polyimides containing bipyridinium triflates. Because trifluoromethane sulfonate (triflate) is known for its thermal stability,[18] bipyridinium-based polyimides with triflate anion are postulated to be more thermally stable.

Experimental Section

Measurements. IR spectra were recorded on a Shimadzu 340 spectrometer. UV−visible spectra were recorded on a Shimadzu UV-3100 recording spectrophotometer. ^{1}H NMR (200 MHz) and ^{13}C NMR (200 MHz) spectra were obtained using a Varian-Unity 200 superconductor NMR spectrometer. Elemental analyses were carried out with a Heraeus CHN-Rapid analyzer. The wide-angle X-ray diffraction patterns were obtained from powder specimens on a MXP18A-HF X-ray diffractometer. Differential scanning calorimeter (DSC) was performed on a Perkin-Elmer 7 series thermal analyzer system in flowing nitrogen (40 cm^3/min) at a heating rate of 20 °C/min. Thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer 7 series thermal analysis system in flowing nitrogen and air (40 cm^3/min) at a heating rate of 20 °C/min. An Instron universal tester model 1122 with a load cell of 5 kg was used to study the stress−strain behavior of the samples. A gauge of 1 cm and a strain rate of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 4 cm long, and ca. 0.05 mm thick); an average of 5 individual determinations was used.

Reagents and Solvents. Pyromellitic dianhydride (PMDA), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), and 4,4′-oxydiphthalic anhydride (ODPA) were recrystallized from acetic anhydride. 4,4′-Diaminobiphenyl ether, (4,4′-diaminodiphenyl)methane, and 4,4′-diaminobiphenyl were recrystallized from ethanol. Acetonitrile was dried by distillation over P_2O_5. Dimethylformamide (DMF) was dried by distillation over P_2O_5 and CaH_2 respectively. Other reagents were used as purchased without further purification.

3,3′-(1,4-Phenylene)bis(1,5-diphenyl-1,5-pentadione) (1). It was prepared according to a reported method[19] in 97% yield, purified by recrystallization from toluene and characterized as follows: mp 205−207 ºC (lit.[19] 205−206 °C). IR (KBr, cm^{-1}): 1680(C═O), 1590, 1440, 1270, 1204.

4,4′-(1,4-Phenylene)bis(2,6-diphenylpyrylium triflate) (2). To the suspension of triphenylmethanol (8.14 g, 0.031 mol) in 92 mL of acetic anhydride was added carefully and slowly 99 wt % of trifluoromethanesulfonic acid (5.93 g, 0.039 mol). The reaction mixture became homogeneous and was maintained at 10−20 °C with a water bath during the exothermic process. Then 3,3′-(1,4-phenylene)bis(1,5-diphenyl-1,5-pentadione) (7.54 g, 0.013 mol) was added to the reaction mixture. After the heterogeneous reaction mixture was stirred at 40 °C overnight, the yellow precipitate was collected by filtration,

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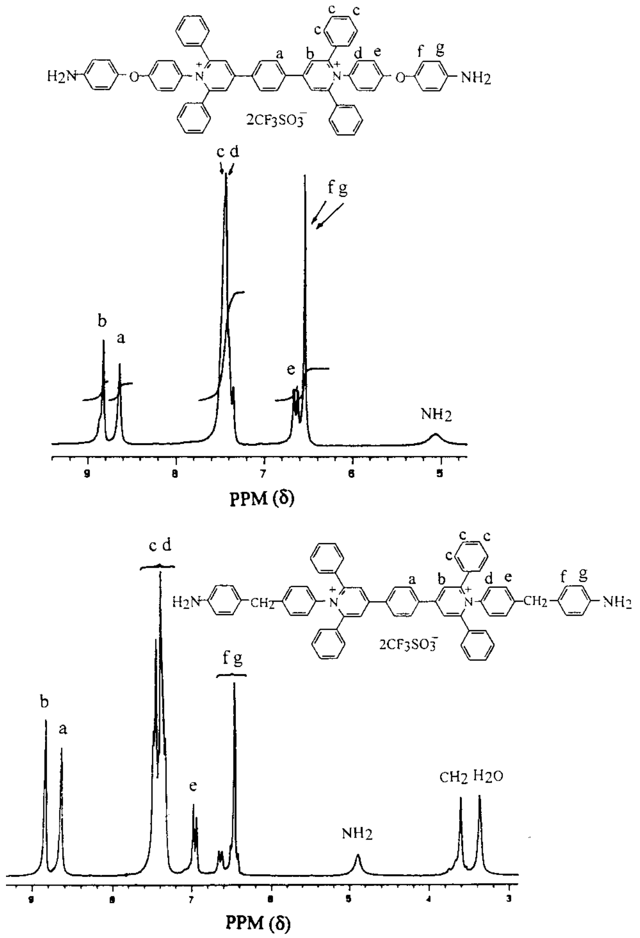


Figure 1. ^{1}H NMR spectra of compounds **3a** and **3b**.

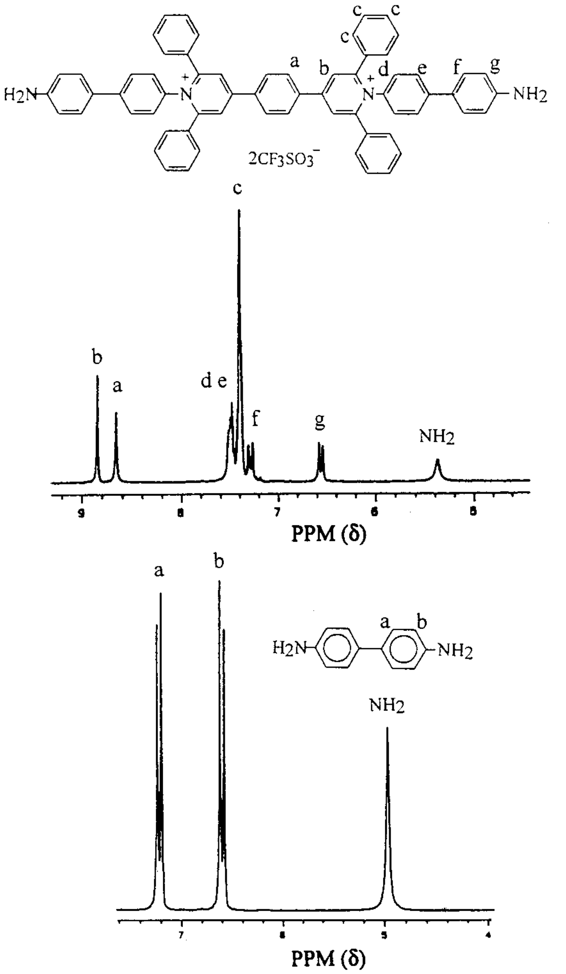


Figure 2. ^{1}H NMR spectra of compound **3c** and 4,4′-diaminodiphenyl.

washed with acetic anhydride and ethanol, and dried in air to afford 10.6 g (97%) of product. IR (KBr, cm^{-1}): 1613 (pyrylium), 1579, 1500, 1465, 1440, 1260 (br, SO_3), 1152 (SO_3), 1030. ^{1}H NMR (DMSO-d_6, δ, ppm): 7.7−9.2 (m, 24H, aromatic); 9.38 (s, 4H, 3,5-aromatic). Anal. Calcd for $C_{42}H_{28}F_6S_2O_8$: C, 60.14; H, 3.36. Found: C, 59.96; H, 3.21.

General Procedure for the Preparation of 1,1′-Diaminoarylidene-4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium triflate) (3). A solution of aromatic diamine (4.6 mmol) and compound **2** (1.66 g, 2 mmol) in 20 mL of acetonitrile was heated at 82 °C under N_2 for 6 h. The reaction mixture remained homogeneous during the entire process. After the mixture was cooled, it was poured into 400 mL of diethyl ether with strong stirring. Yellow or brown red product was collected by filtration and dried under N_2 with average yield of 90%.

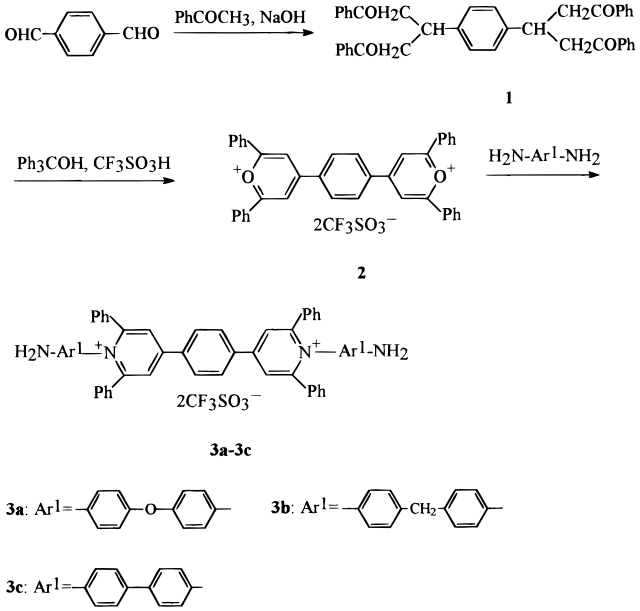
1,1′-Bis(4-(4-aminophenyleneoxy)phenylene)-4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium triflate) (3a). IR (KBr, cm^{-1}): 3450, 3320, 1615 (pyridinium), 1495, 1260 (br, SO_3), 1150 (SO_3), 1025. The assignment of the ^{1}H NMR (DMSO-d_6, δ, ppm) spectra is shown in Figure 1: 8.83 (s, 4H, aromatic), 8.64 (s, 4H, aromatic), 7.44−7.35 (m, 24H, aromatic), 6.67 (d, J = 8.8 Hz, 4H, aromatic), 6.45 (m, 8H, aromatic), 5.07 (broad, $-NH_2$). ^{13}C NMR (DMSO-d_6, δ, ppm): 159.21, 156.84, 145.83, 144.97, 136.73, 133.22, 133.00,130.36, 130.01, 129.91, 128.22, 125.73, 120.53, 116.40, 114.93. Anal. Cald for $C_{66}H_{48}N_4F_6S_2O_8$: C, 65.88; H, 4.02; N, 4.66. Found: C, 65.69; H, 3.99; N, 4.48.

1,1′-Bis(4-(4-aminophenylenemethylene)phenylene)-4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium triflate) (3b). IR (KBr, cm^{-1}): 3450, 3350, 1614 (pyridinium), 1500 (m), 1260 (br, SO_3), 1150 (SO_3), 1030. The assignment of the ^{1}H NMR (DMSO-d_6, δ, ppm) spectra is shown in Figure 1: 8.83 (s, 4H, aromatic), 8.64 (s, 4H, aromatic), 7.34−7.49 (m, 24H, aromatic), 6.96 (d, J = 8.8 Hz, 4H, aromatic), 6.55 (dd, J_1 = 9.64 Hz, J_2 = 38.55 Hz, 4H, aromatic), 6.47 (s, 4H, aromatic), 4.89 (broad, $-NH_2$), 3.60 (s, 4H, $-CH_2-$). ^{13}C NMR (DMSO-d_6, δ, ppm): 156.63, 154.02, 146.66, 143.86, 136.98, 136.82, 133.17, 129.96, 129.88, 129.09, 128.56, 128.12, 127.47, 125.71, 114.00, 39.87. Anal. Cald for $C_{68}H_{52}N_4F_6S_2O_8$: C, 68.10%; H, 4.37%; N, 4.67%. Found: C, 67.94%; H, 4.21%; N, 4.22%.

1,1′-Bis(4-(4-aminophenylene)phenylene)-4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium triflate) (3c). IR (KBr, cm^{-1}): 3500, 3350, 1616 (pyridinium), 1490, 1260 (br, SO_3), 1150 (SO_3), 1030. The ^{1}H NMR (DMSO-d_6, δ, ppm) spectrum is shown in Figure 2: 8.85 (s, 4H, aromatic), 8.66 (s, 4H, aromatic), 7.53−7.48 (m, 20H, aromatic), 7.40−7.38 (m, 8H, aromatic), 7.29 (d, J = 8.6 Hz, 4H, aromatic), 6.57 (d, J = 8.6 Hz, 4H, aromatic), 5.38 (broad, $-NH_2$). ^{13}C NMR (DMSO-d_6, δ, ppm): 156.71, 153.95, 149.28, 141.32, 136.81, 136.58, 133.24, 130.01, 129.85, 128.94, 120.18, 127.28, 125.80, 124.45, 124.41, 114.14. Anal. Cald for $C_{66}H_{48}N_4F_6S_2O_8$: C, 67.68; H, 4.13; N, 4.78. Found: C, 66.89; H, 4.10; N, 4.56.

Polymerization. A general polymerization procedure is described as follows. A solution of the 1,1′-diaminoarylidene-4,4′-(1,4-phenylpyridinium triflates) **3** (0.5 mmol) and aromatic tetracarboxylic dianhydrides **4** (0.5 mmol) in 5 mL of DMF was stirred at room temperature for 4 h to afford a brown red sticky poly(amic acid). The inherent viscosity of the resulting poly(amic acid) in DMF was measured at a concentration of 0.5 g/dL at 25 °C. The poly(amic acid) solution was spread on a glass plate and heated at 65 °C to evaporate the solvent. The imidization was carried out by sequential heating at 100, 200, and 280 °C for 1 h each. The resulting polyimide films were removed from the glass plate by soaking in water. The inherent viscosity of the polyimide was measured in DMF at a concentration of 0.5 g/dL at 25 °C.

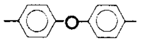
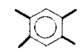
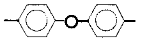
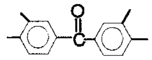
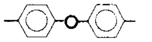
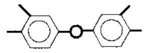
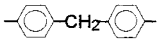
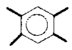
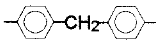
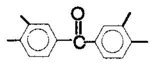
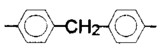
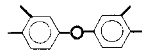
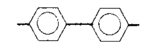
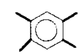
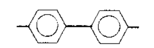
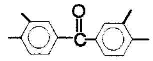
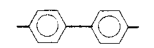
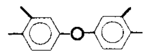
Scheme 1



Results and Discussion

Monomer Synthesis. The monomer 1,1′-bis(aminoarylidene)-4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium triflate) **3** was synthesized according to the reaction sequence of Scheme 1. Tetraketone **1** was prepared by a reported method[19] and was quantitatively cyclodehydrated to bis(pyrylium triflate) **2** with trifluoromethanesulfonic acid. Because the acidity of trifluoromethanesulfonic acid is much stronger than that of perchloratic acid,[18] this cyclodehydration reaction proceeded more smoothly and completely than the reaction with perchloratic acid. ^{1}H NMR spectroscopy and elemental analyses verified the purity of **2** which was directly obtained from reaction mixture was rather satisfied. Bis(pyrylium triflate) **2** reacted with excess aromatic diamines in acetonitrile at 60 °C to form a pyridinium ring. The ring transformation proceeded much faster than the reaction with bis(pyrylium perchlorate). The reaction mixture remained homogeneous during the entire process. Compounds **3a**−**c** were filtered after precipitation by diethyl ether. Compounds **3a**−**c** were characterized by NMR spectroscopy as well as IR and elemental analyses. The purity of monomers was rather good by evaluation of ^{1}H NMR. ^{1}H NMR peak assignments of them are given in Figures 1 and 2. Amino groups of all three compounds show chemical shifts near 5 ppm. Although the amino group of **3c** had the largest chemical shift for amino at 5.35 ppm due to the electron-withdrawing effect of pyridinium, the difference among them was not very big compared to that for **3a** and **3b**. The chemical shift of protons labeled **f** and **g** of **3c** were 6.55 and 7.28 ppm. These were similar to the chemical shifts of protons labeled **a** and **b** for 4,4′-diaminobiphenyl at 6.50 and 7.21 ppm, respectively. These indicated that the electron-withdrawing effect of pyridinium was not as strong as on the terminal phenyl of **3c**. It was reported that the side phenyls were almost coplanar with the pyridinium ring and caused a significant steric hindrance on the N-substituent group. Therefore, it was impossible for the *N*-aryl group to be coplanar with the pyridinium ring. Additionally, *N*-aryl group could barely conjugate with the pyridinium ring. As the result, the electron-withdrawing effect was not significant on the terminal phenyl group of **3c.**

Table 1. Polyimides Containing Bipyridinium Triflates

polyamic acid	Polyimide	Ar^1	Ar^2
5a	6a		
5b	5b		
5c	6c		
5d	6d		
5e	6e		
5f	6f		
5g	6g		
5h	6h		
5i	6i		

Polymerizations. The bis(aminoarylidenepyridinium triflate) **3** was polymerized with equimolar equivalents of various aromatic dianhydrides **4** in DMF at ambient temperature (Scheme 2). This afforded poly(amic acid) **5**. The inherent viscosities ranged from 0.73 to 1.17 dL/g (Table 2). Monomer **3c** still had high reactivity with aromatic tetracarboxlic anhydrides.

The polyimide films **6** were obtained by a thermal cyclodehydration procedure and their inherent viscosities were between 0.31 and 0.58 dL/g in DMF at 25 °C. Creasable tough films could be obtained after imidization, which indicates the formation of high molecular weight polymers. The elemental analyses of these polyimides agreed well with the theoretical values (Table 2). The characteristic IR absorption for amic acid around 3350 and 1650 cm^{-1} (except polyimides derived from BTDA) disappeared completely, while the characteristic imide IR absorption around 1780, 1120 and 740 cm^{-1} appeared.

Properties of Polyimides. The solubilities of the polyimides were tested qualitatively in various solvents. The results are given in Table 3. All polymers displayed outstanding solubility in the most of tested solvents. They could be well dissolved even in less efficient solvents such as pyridine and acetonitrile except **6h** because of its extremely rigid structure. **6a**−**d** and **6f** could be partially dissolved in acetone, while **6c** and **6f** could be partially dissolved in cyclohexanone. Polymers with flexible linkages such as oxygen were more solube than those with rigid linkage. Although polymers derived from PMDA are more rigid than those derived from BTDA, the former had better solubility than the latter. This was attributed to the relatively high ion pair density along the backbone of the polymers derived from PMDA. On the basis of our previous work, the solubility of the polyimides containing 2,2-bipyridine

Scheme 2

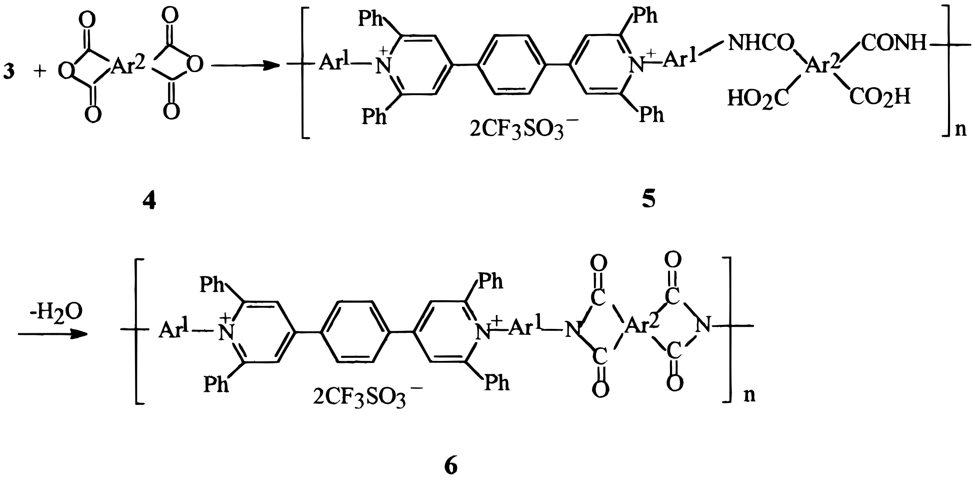


Table 2. Inherent Viscosities and Elemental Analyses of Polymers

poly(amic acid)	ηinh (dL/g)[a]	polyimide	ηinh (dL/g)[a]	elemental analyses of polyimides[b] (%) C	H	N
5a	1.17	**6a**	0.43	64.87	3.47	3.58
				(65.89)	(3.35)	(4.04)
5b	1.09	**6b**	0.57	66.42	3.49	3.42
				(66.93)	(3.38)	(3.76)
5c	0.73	**6c**	0.45	66.38	3.65	3.65
				(66.66)	(3.41)	(3.79)
5d	1.17	**6d**	0.41	67.51	3.93	4.00
				(67.82)	(3.65)	(4.06)
5e	0.92	**6e**	0.49	68.36	3.91	3.59
				(68.73)	(3.66)	(3.77)
5f	1.35	**6f**	0.48	68.02	3.85	3.46
				(68.47)	(3.69)	(3.80)
5g	1.05	**6g**	0.31	66.77	3.62	4.16
				(67.45)	(3.43)	(4.14)
5h	1.93	**6h**	0.58	67.50	3.66	3.54
				(68.40)	(3.46)	(3.84)
5i	1.81	**6i**	0.37	67.30	3.54	3.71
				(68.14)	(3.49)	(3.88)

[a] Inherent viscosity in DMF (0.5 g/dL) at 25 °C. [b] Data in parentheses are the calculated values.

groups will be significantly improved even by partial quaternization of the pyridine group.[20] It is obvious that the ion pair plays a very important role in the significant improvement of solubility. The basicity of triflate anion is weaker than that of perchlorate anion. All the polyimides with triflate anions had better solubility in common organic solvents than those containing perchlorate anions. A lyotropic behavior was observed in a 20 wt %/wt solution of polymers in DMF or NMP at ambient temperature.

Wide-angle X-ray diffraction was used to characterize the structure of polymers. **6c** and **6g** with the most flexible and rigid structure respectively were employed as the samples. As shown in Figure 4, they were basically amorphous and gave out two broad diffraction peaks at 10.6 and 18.4°, indicating a crystalline pattern. The peak located at a relatively low-angle region was indicative of long-range order.[20] Most of their crystalline pattern should be attributed to a short-range one.

The thermal behavior of the polymers was evaluated by differential scanning calorimeter (DSC) and thermogravimetric analyses (TGA). However, either glass transition temperatures or melting endotherms could not be obtained in DSC thermograms below 400 °C. All polyimides underwent 5% weight losses between 459 and 478 °C in nitrogen and between 469 and 489 °C in air. Their decomposition temperatures were almost 100 °C higher than those of polyimides containing perchlorate anions (Figure 5). Their decomposition also underwent two stages. This suggests that the decomposition of triflate anion occurs at the beginning of the polymer's decomposition. Generally speaking the thermal stability of polyimides is much better than their thermo-oxidative stability. However, the thermo-oxidative stability of these polymers was higher than their thermal stability. It was reasonable to conjecture that the decomposition of anions involved a charge transfer from anion to bipyridinium. This charge-transfer process would be hindered by O_2 in air.[21]

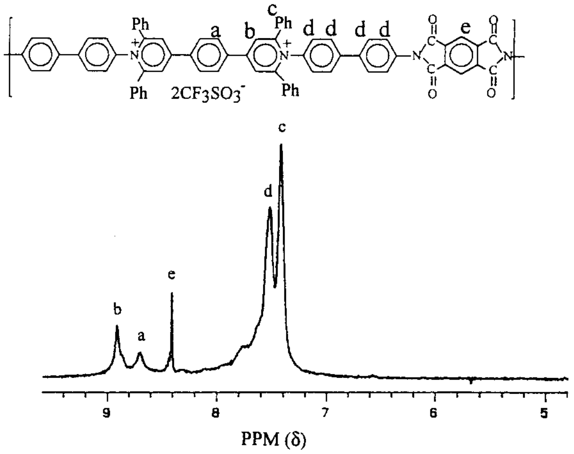


Figure 3. ^{1}H NMR spectra of polymer **6g**.

The tensile properties of the polyimide films are summarized in Table 4. **6d** and **6g** could not be cast into flexible films due to their rigid nature. Their tensile strengths were between 59 and 93 MPa; elongations at break were between 5 and 9%. Most of them exhibited a high tensile strength and a low elongation.

The polymers with rigid-rod structure could be well dispersed in a flexible polymer like poly(vinylpyrrolidone) (PVP). Transparent films obtained from the mixture of PVP and these polyimides implied good compatibility between them. Sandwiches of polyimides in NMP or DMF as well as polyimide−PVP films could reversibly develop color under UV irradiation. The UV−visible spectra of polymers were different from monomers **3** upon irradiation (Figures 6 and 7). The

Table 3. Solubilities of Polymers[a]

	solvents[b]								
polymer	DMSO	DMF	NMP	m-cresol	H_2SO_4	Py	AN	acetone	CH
6a	++	++	++	+	+	++	++	+−	−
6b	++	++	++	+	+	++	+	+−	−
6c	++	++	++	+	++	++	+−	+−	+−
6d	++	++	++	+	+	+	+	−	−
6e	++	++	++	+	+	++	++	+−	−
6f	++	++	++	+	+	++	++	+−	+−
6g	++	++	++	+	+	+	+−	−	−
6h	++	++	++	+	+	−	−	−	−
6i	++	++	++	+	+	+	+	−	−

[a] Solubility: ++, soluble at room temperature; +, soluble in hot solvent; +−, partially soluble; −, insoluble. [b] DMSO, dimethyl sulfoxide; DMF, *N*,*N*-dimethylforamide; NMP, *N*-methylpyrrolidone; Py, pyridine; AN, acetonitrile; CH, cyclohexane.

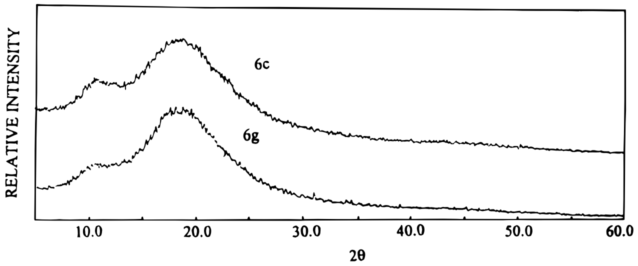


Figure 4. Wide-angle X-ray diffractograms of polymer **6c** and **6g**.

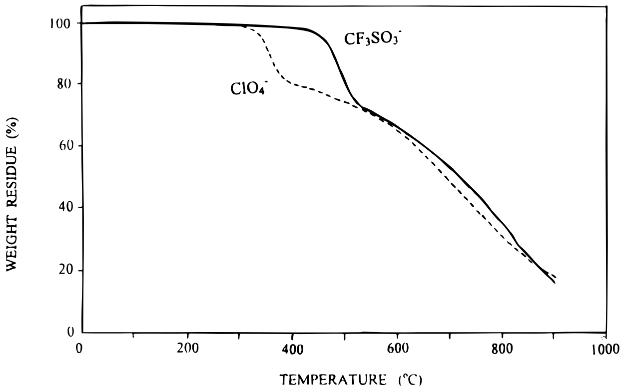


Figure 5. TGA thermograms of polymer 6a and corresponding polymer with perchlorate as anion in nitrogen with a heating rate of 20 °C/min.

Table 4. Thermal and Mechanical Properties of Polymers

	dec temp (°C)[a]		tensile strength	elongation at
polymer	in air	in N_2	(MPa)	break (%)
6a	484	477	84	6
6b	477	468	93	6
6c	488	471	74	9
6d	475	467	*b*	*b*
6e	469	459	61	8
6f	472	460	59	9
6g	485	478	*b*	*b*
6h	485	468	75	5
6i	489	478	88	5

[a] Temperature at which 5% weight loss was recorded on TGA at a heating rate of 20 °C/min. [b] Could not be determined due to the brittleness of the film.

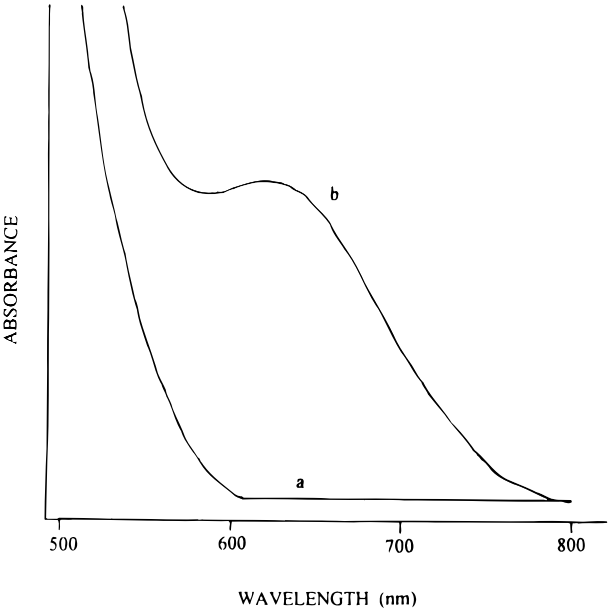


Figure 6. Typical UV−visible spectrum of compounds **3** in PVP matrix before (a) and after (b) UV irradiation.

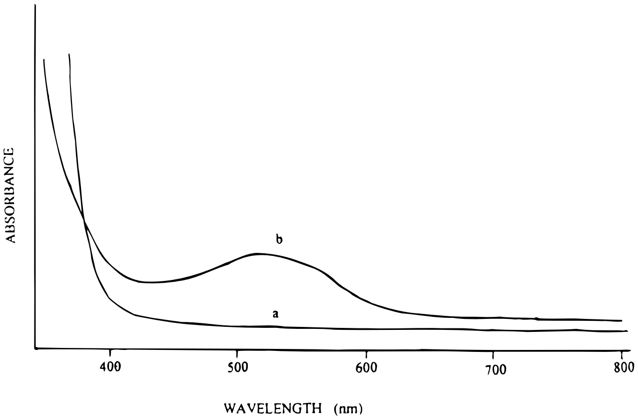


Figure 7. A typical UV−visible spectrum of polymer **6** in solution of NMP before (a) and after (b) UV irradiation.

absorption peak of **3** appeared at about 620 nm, which is consistent with characteristic absorption of a bipyridinium radical cation. Although substituted with *N*-aryl groups, no red shift in absorption band was observed.[22,23] This phenomena confirmed to that *N*-aryl groups did not conjugate with the pyridinium ring. This was due to the steric hindrance of side phenyls. The only absorption peak in the visible region of the UV-visible spectrum was at about 512 nm and was attributed to the aggregation of radical cation pairs of bipyridinium. It was generally considered that side substituent groups would prevent aggregation of radical cation pairs. These bipyridinium-based polyimides with four bulky phenyls as substituents formed only radical dimers after irradiation. This may resulted from the lyotropic behavior of polymers in NMP and DMF solution. It was mentioned above that the bipyridinium ring was coplanar with four substituent phenyls. The formation of radical dimers could be achieved when polymer chains pack parallel to the coplane of the bipyridinium.[24]

Conclusions

A new series of bipyridinium triflate based aromatic diamines were successfully prepared and used as starting materials for the preparation of ionic polyimides. These polyimides were soluble in polar aprotic solvents. Although they were basically amorphous, no glass transition temperature was detected by DSC. The thermal and thermooxidative stabilities of these polyimides were greatly improved using triflate anions. They were fairly thermally stable up to 469−489 °C in air. Furthermore, the films of these polyimides displayed good tensile properties. They also could reversibly develop color under irradiation both in solution and in the polymer matrix.

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