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Synthesis of soluble polyimides containing bipyridinium dihydrogen phosphate and *p*-toluenesulfonate and effect of anions on properties of polyimides

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Abstract

The objective of this research was to investigate the effect of anions on the properties of soluble polyimides containing bipyridinium salt. Thus the work began with the synthesis of two new diamines: 1,1′-di[4-(4-aminophenoxy) phenyl]-4,4′-(1,4-phenylene)bis(2,6-diphenyl pyridinium dihydrogen phosphate) and 1,1′-di[4-(4-aminophenoxy)phenyl]-4,4′-(1,4-phenylene)bis(2,6-diphenyl pyridinium *p*-toluenesulfonate). The two new diamines were polymerized with several dianhydrides to afford two new series of soluble polyimides. The polyimides have inherent viscosities that range from 0.284 to 0.449 dl g^{-1} in *N,N*-dimethylformamide at 25°C. These new polymers are soluble in polar aprotic solvents. Polymers containing $H_2PO_4^-$ show no glass transition temperature (T_g) and the T_gs of polymers containing *p*-toluenesulfonate (PTS$^-$) are around 240°C. Thermogravimetric analysis showed that the polymers began to decompose in the range from 390 to 419°C. Studies showed that the solubility, T_gs, thermal stabilities, absorption in the visible region and photosensitivities of the polymers were affected by the basicity, structure, thermal stabilities and soft/hard character of the anions, respectively. © 1998 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Soluble polyimides; Bipyridinium; Counter anions

1. Introduction

Polyimides have been studied extensively as high-performance materials for applications in integrated electronic circuits and aerospace devices as a consequence of their exceptional thermal, mechanical, optical and dielectric properties [1,2]. However, the technological applications of many polyimides are somewhat limited by processing difficulties owing to their insolubility in organic solvents and extremely high glass transition, softening or melting temperature [3]. Therefore, the preparation of soluble or thermoplastic polyimides has been a major interest in research work. Current and prior attempts to produce soluble and processable aromatic polyimides involved the introduction of flexible linkages [4–6] or molecular asymmetry [7,8] into the backbone, or the addition of bulky side groups [9,10]. Some special groups such as cardo and naphthalene were also incorporated into the polymer backbone to improve their solubility in organic solvents with considerable success [11–14]. Very recently, we successfully synthesized soluble polyimides containing bipyridinium perchlorate and triflate by a facile method [15,16]. Bipyridinium, known as viologen, is a kind of redox compound. Polymers containing the viologen moiety belong to the class of ionic polymers named ionenes [17]. Viologen polymers have considerable potential for use in materials for modified electrodes [18–20], photo-assisted hydrogen evolution [21] and organic synthesis [22], photochromic materials [23,24], electron-transfer membranes [25], anion-exchange membranes [26], etc. The bipyridinium-based polyimides have enhanced solubility without decreasing the rigidity of their backbone and are functionlized by the viologen moiety. They displayed photochromic behaviour in *N*-methylpyrrolidone (NMP) solution. However, we found that these bipyridinium-based polyimides containing different anions display different thermal stability and solubility. Two new kinds of bipyridinium-based polyimide, containing dihydrogen phosphate and *p*-toluenesulfonate, were synthesized in this work to further investigate the effect of anions on the properties of the polymers.

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2. Experimental

2.1. Instrumentation

Proton nuclear magnetic resonance (^{1}H-n.m.r.) spectra were measured at 200 MHz on a Varian Unity Superconductor spectrometer. Infra-red (i.r.) spectra were recorded on a Shimadzu 340 spectrometer. Ultraviolet (u.v.) and visible spectra were obtained with a Hitachi 430 spectrophotometer. Elemental analyses were performed by a Heraeus CHN rapid analyser. Inherent viscosities were determined on a Cannon–Ubbelohde viscometer for solutions of 0.5 g dl^{-1} at 25°C. Wide-angle X-ray diffraction patterns were obtained for film specimens on an MXP18A-HF X-ray diffractometer. Thermogravimetric analysis (t.g.a.) and differential scanning calorimetric (d.s.c.) analysis were recorded in nitrogen and air with a Perkin–Elmer 7 Series thermal analyser at a heating rate of 20°C min^{-1}.

2.2. Monomers

2.2.1. 3,3′-(1,4-Phenylene)bis(1,5-diphenyl-1,5-pentadione) (3)

The compound **3** was prepared according to a reported method and characterized as follows. M.p. 205–207°C (lit. [27] m.p. 205–206°C). I.r. (KBr), ν (cm^{-1}): 1680 (C=O), 1590, 1440, 1270, 1204.

2.2.2. Triphenylmethyl hexfluorophosphorate

To the solution of triphenylmethanol (26 g, 0.1 mol) in 180 ml of acetic anhydride was added carefully 12 ml of 60 wt% hexafluorophosphoric acid dropwise. The reaction mixture became homogeneous and then heterogeneous again. The reaction mixture was maintained at 10–20°C with a water bath during the exothermic process and stirred at this temperature for 2 h. The orange crystals were collected by filtration and washed with diethyl ether to afford 32.5 g (84%) of product.

2.2.3. 4,4′-(1,4-Phenylene)bis(2,6-diphenylpyrylium dihydrogen phosphate) (5)

A mixture of triphenylmethyl hexafluorophosphorate (9.13 g, 0.024 mol) and compound **3** (5.78 g, 0.01 mol) was stirred vigorously in 60 ml of acetic acid and heated at reflux for 4 h. After the reaction mixture was cooled to ambient temperature, the precipitate **4** was collected by filtration and washed with ethanol. Then hydrolysis of bispyrylium hexafluorophosphorate **4** was carried out in refluxing formic acid for 2 h. The resulting yellow crystals were obtained by filtration to afford 4.5 g (74%) of product **5**. I.r. (KBr), ν (cm^{-1}): 1610 (pyrylium) 1575, 1500, 1465, 1440, 1260, 1220, 1150 cm^{-1} (broad, PO_4^{3-}). ^{1}H-n.m.r. [deuterated dimethyl sulfoxide (DMSO–d_6)], δ (ppm): δ 9.35 (s, 4H, 3,5-aromatic), 9.21–7.56 (m, 24H, aromatic). Analysis calculated for $C_{40}H_{32}O_{10}P_2$: C, 65.40; H, 3.49. Found: C, 65.83; H, 3.33.

*2.2.4. 1,1′-Di[4-(4-aminophenoxy)phenyl]-4,4′-(1,4-phenylene)bis(2,6-diphenyl pyridinium dihydrogen phosphate) (**6**)*

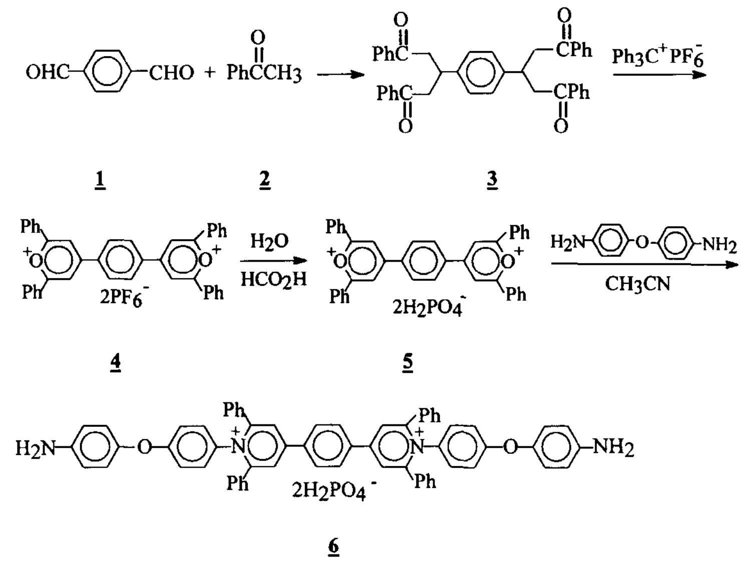
A solution of 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium dihydrogen phosphate) **5** and 4,4′-diaminodiphenyl ether (1.00 g, 0.005 mol) in 42 ml of acetonitrile was heated at 80°C for 6 h under nitrogen. A yellow precipitate formed during the process. After the resulting reaction mixture was poured into 300 ml of diethyl ether with stirring, the precipitate was collected by filtration and dried under nitrogen to yield 2.22 g (94%) of yellow powder. I.r. (KBr), ν (cm^{-1}): 1609 (pyridinium), 1487, 1210, 1045 (broad, PO_4^{3-}). ^{1}H-n.m.r. (DMSO–d_6), δ (ppm): 8.83 (s, 4H, 3,5-pyridinium), 8.64 (s, 4H, phenylene), 7.45 (m, 20H, 2,6-phenyl), 7.35 (d, J = 9.2 Hz, 4H, 1-phenyl), 6.64 (d, J = 9.0 Hz, 4H, 1-phenyl), 6.53 (s, 8H, aminophenoxy), 3.40 (broad, amino). Analysis calculated for $C_{64}H_{52}N_4O_{12}P_2$: C, 64.32; H, 4.05; N, 4.69. Found: C, 64.38; H, 3.87; N, 4.61.

2.2.5. 4,4′-(1,4-Phenylene)bis(2,6-diphenylpyrylium p-*toluenesulfonate) (7)*

Triphenylmethanol (5.2 g, 0.02 mol) and *p*-toluenesulfonic acid (3.44 g, 0.02 mol) were added to 58 ml of acetic anhydride, followed with stirring at room temperature for 3 h. Then 3,3′-(1,4-phenylene)bis(1,5-diphenyl-1,5-pentadione) **3** (4.8 g, 0.008 mol) was added to the reaction mixture and the mixture was heated to 100°C for 1 h. The heterogeneous mixture became clear. Upon cooling yellow crystals appeared and were collected by filtration, washed carefully with acetic anhydride and ethanol, respectively, and dried in air to afford 6.92 g (94%) of yellow powder. I.r. (KBr), ν (cm^{-1}): 1605 (pyrylium), 1575, 1500, 1462, 1440, 1260, 1200 (SO_3), 1120, 1032, 1010. ^{1}H-n.m.r. (DMSO–d_6), δ (ppm): 9.35 (s, 4H, 3,5-aromatic), 9.21–7.56 (m, 24H, aromatic), 7.47 (d, J = 8.0 Hz, 4H, toluene-H), 7.086 (d, J = 7.8 Hz, 4H, toluene-H), 2.67 (s, 6H, $-CH_3$). Analysis calculated for $C_{54}H_{42}O_8S_2$: C, 73.45; H, 4.79. Found: C, 72.98; H, 5.01.

2.2.6. 1,1′-Di[4-(4-aminophenoxy)phenyl]-4,4′-(1,4-phenylene)bis(2,6-diphenyl pyridinium p-*toluenesulfonate) (8)*

A solution of 4,4′-(1,4-phenylene)bis(2,6-diphenyl pyrylium *p*-toluenesulfonate) **7** (1.70 g, 0.002 mol) and 4,4′-diaminodiphenyl ether in 15 ml of *N,N*-dimethylformamide (DMF) was heated at 45°C under nitrogen for 4 h. The reaction mixture remained homogeneous during the entire process. The resulting solution was poured into a large excess of diethyl ether (400 ml) with rapid stirring. The pale yellow precipitate was collected by filtration and dried in nitrogen to yield 2.5 g (86%) of product. I.r. (KBr), ν (cm^{-1}): 1612 (pyridinium), 1490, 1220, 1190 (SO_3), 1120, 1032, 1010. ^{1}H-n.m.r. (DMSO–d_6), δ (ppm):



Scheme 1.

8.82 (s, 4H, 3,5-pyridinium), 8.64 (s, 4H, phenylene), 7.46 (broad, 24H, 2,6-phenyl and toluene-H), 7.40 (d, $J = 8.8$ Hz, 4H, 1-phenyl), 7.12 (d, $J = 6.5$ Hz, 4H, toluene-H), 6.65 (d, $J = 8.8$ Hz, 4H, 1-phenyl), 6.55 (s, 8H, aminophenoxy), 5.27 (broad, amino), 2.27 (s, 6H, $-CH_3$). Analysis calculated for $C_{78}H_{62}N_4O_8S_2$: C, 75.10; H, 5.10; N, 4.49. Found: C, 74.98; H, 4.98; N, 4.61.

2.3. Polymer syntheses

The dianhydride (0.5 mmol) was added to a solution of the diamine **6** or **8** (0.5 mmol) in 5 ml of DMF and then the solution was stirred at ambient temperature for 4 h to afford 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^{-1} 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°C, 200°C and 250°C for 1 h each. The inherent viscosity of the polyimide was measured in DMF at a concentration of 0.5 g dl^{-1} at 25°C.

3. Results and discussion

3.1. Monomer syntheses

The monomer **6** was synthesized according to the reaction

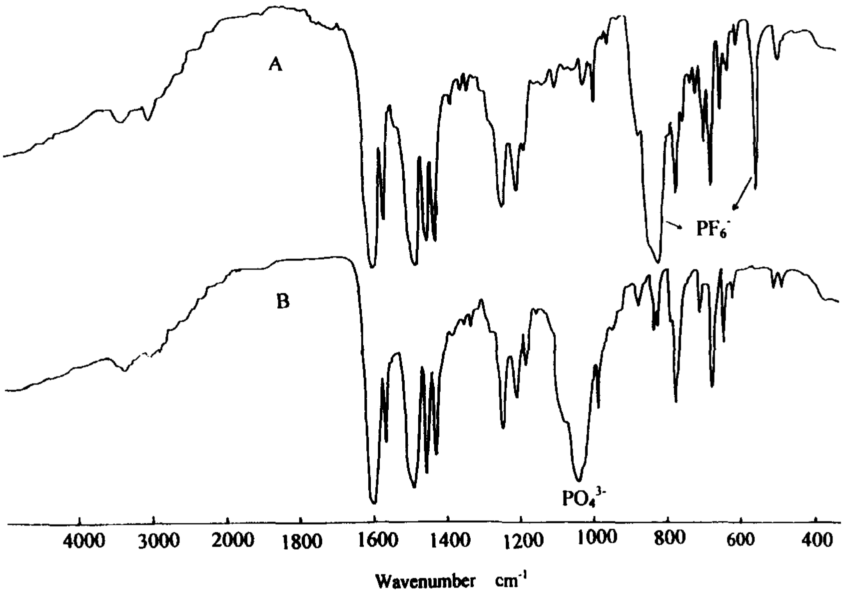
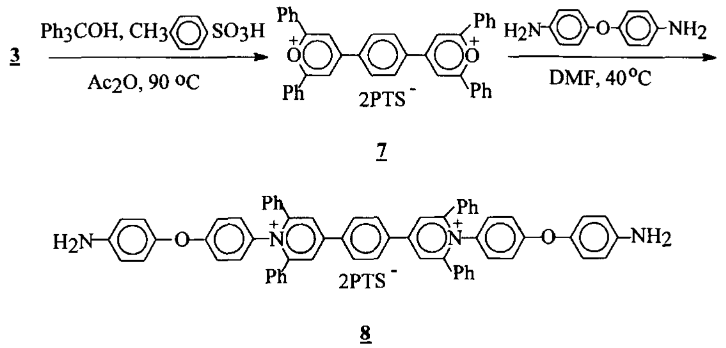


Fig. 1. Change in the i.r. spectra of 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium hexafluorophosphorate) (**4**) before (A) and after (B) hydrolysis in formic acid.



Scheme 2.

sequence of Scheme 1. Compound **3** was prepared by a reported method [27]. Bis(pyrylium dihydrogen phosphate) **5** could not be synthesized directly from phosphoric acid because the main product was the monopyrylium salt. The tetraketone **3** was cyclodehydrated to 4,4′-(1,4-phenylene)-bis(2,6-diphenylpyrylium hexafluorophosphorate) **4** by treatment with triphenylmethyl hexafluorophosphorate in refluxing acetic acid according to the procedure of bis(pyrylium perchlorate). Then the bis(pyrylium hexafluorophosphorate) was completely hydrolysed in refluxing formic acid containing about 15 wt% water. After hydrolysis, the absorption bands of **4** at 820 and 550 cm^{-1} for PF_6^- disappeared and a characteristic phosphoric absorption band at 1045 cm^{-1} appeared in i.r. spectra (Fig. 1). Elemental analysis also demonstrated that the hydrolytic product was bis(pyrylium dihydrogen phosphate). Although the purity of bis(pyrylium hexafluorophosphorate) **4** was unsatisfactory, the purity of its hydrolytic product **5** was rather good. The reaction of **5** and excess 4,4′-diaminodiphenyl ether was carried out in acetonitrile (AN) at 82°C and the pale yellow product **6** precipitated from the solution during the process.

Monomer **8** was prepared by the synthetic route shown in Scheme 2. 4,4′-(1,4-Phenylene)bis(2,6-diphenylpyrylium *p*-toluenesulfonate) **7** was obtained by cyclodehydration of tetraketone **3** with triphenylmethyl *p*-toluenesulfonate which was generated in situ from triphenylmethanol and *p*-toluenesulfonic acid in acetic anhydride, because triphenylmethyl *p*-toluenesulfonate dissolved well in acetic anhydride. The cyclodehydration occurred only when the reaction temperature was above 90°C, at which the reaction mixture became homogeneous. Upon cooling, yellow crystals were deposited from the reaction mixture. The reaction of **7** and 4,4′-diaminodiphenyl ether was much easier than that of pyryliums with other anions. It was carried out in DMF at 45°C. When the reaction proceeded in acetonitrile, the resulting bipyridinium salt was reduced to pyridinium radical cation and the radical cation precipitated from the reaction mixture.

Compounds **6** and **8** were characterized by i.r. and ^{1}H-n.m.r. spectra. The assignment of peaks for their ^{1}H-n.m.r. are given in Figs 2 and 3. Although aromatic protons of bipyridinium **6** have similar chemical shifts to those of the corresponding protons of **8**, amino protons of **6** appeared at 3.40 ppm while amino protons of **8** appeared at 5.27 ppm.

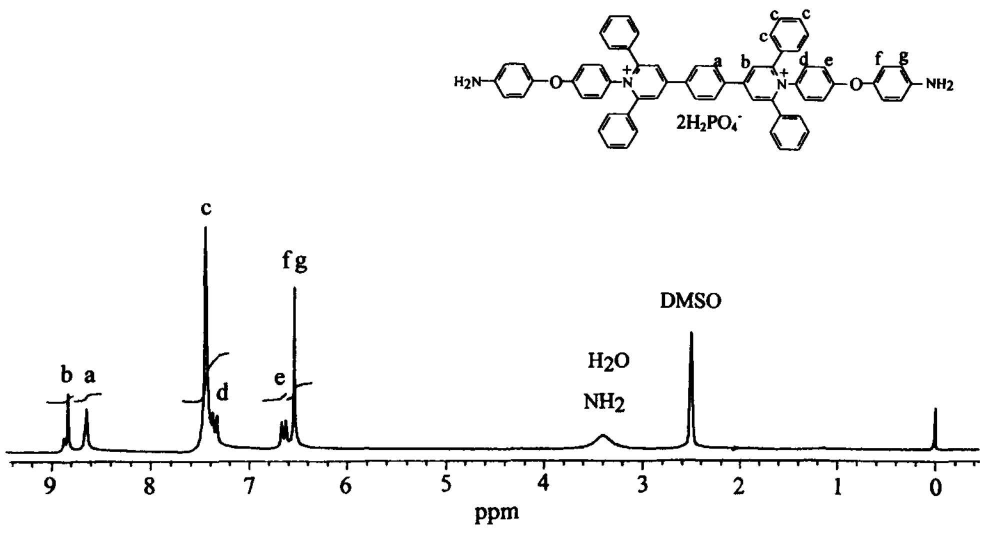


Fig. 2. ^{1}H-n.m.r. spectrum (DMSO-d_6) of 1,1′-di[4-(4-aminophenoxy) phenyl]-4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium dihydrogen phosphate) (**6**).

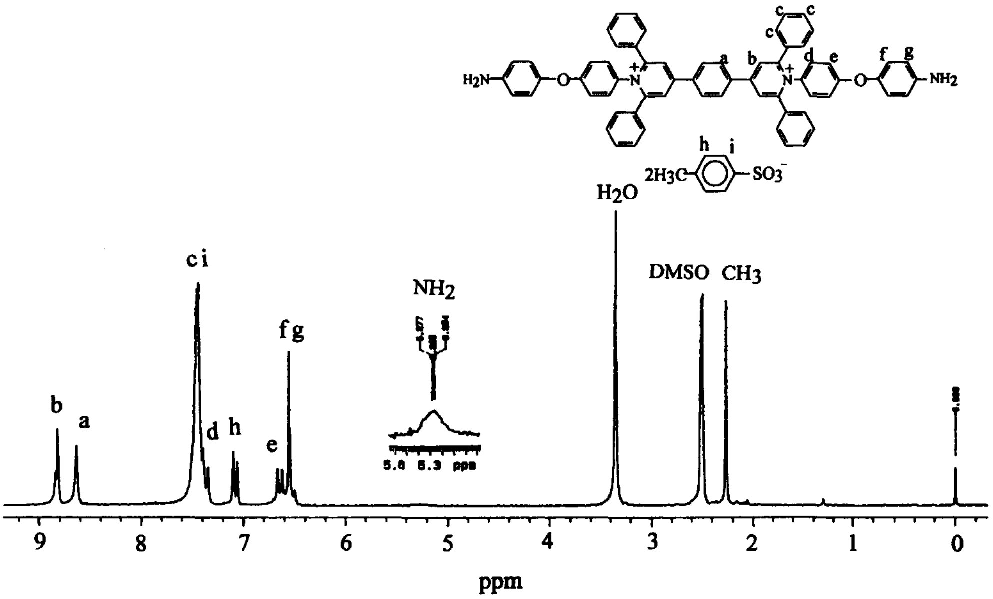
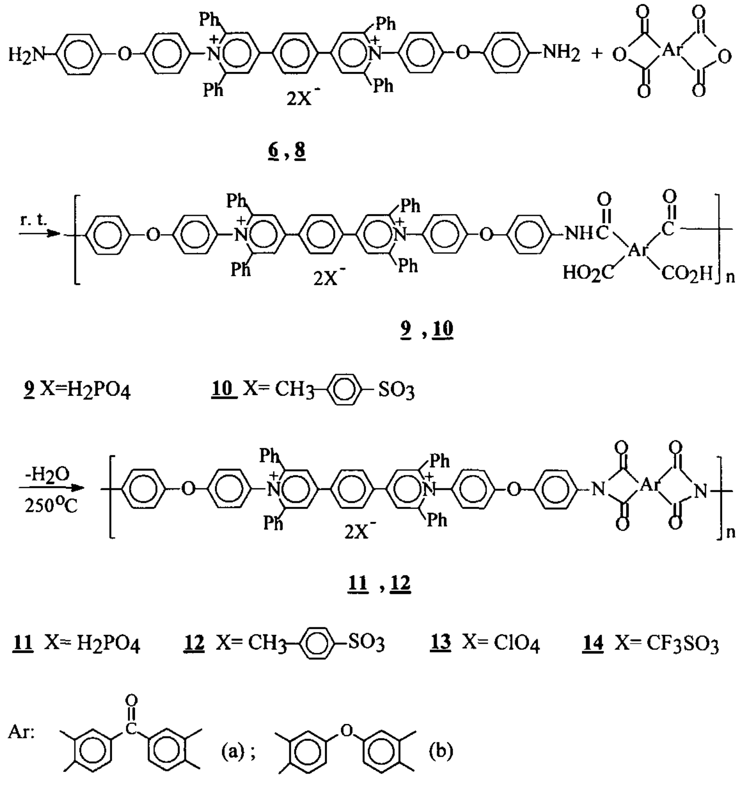


Fig. 3. ^{1}H-n.m.r. spectrum (DMSO-d_6) of 1,1′-di[4-(4-aminophenoxy) phenyl]-4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium *p*-toluenesulfonate) (**8**).

3.2. Polymer syntheses

Monomers **6** and **8** were polymerized with 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4′-oxydiphthalic anhydride (ODPA) in DMF (Scheme 3). The polymerization was carried out at ambient temperature for 4 h. The reaction of **6** with aromatic anhydride was much faster than that of **8**. The resulting poly(amic acid) solution **9** was much more viscous than that of **10** (Table 1) due to dihydrogen phosphate, which could also participate in the formation of hydrogen bonds with carboxy and amide groups. Transparent and flexible films of poly(amic acid)s could be obtained by casting from the resulting polymer solutions. The thermal conversion to polyimides was carried



Scheme 3.

Table 1
Synthesis of poly(amic acid)s and polyimides containing bipyridinium

Poly(amic acid)		Polyimide		Elemental analyses (%)[b]		
Code	η_{inh} (dl g^{-1})[a]	Code	η_{inh} (dl g^{-1})[a]	C	H	N
9a	3.12	**11a**	0.284	69.12 (70.23)	4.15 (3.90)	4.17 (4.05)
9b	3.08	**11b**	0.449	68.42 (69.67)	3.61 (3.64)	3.82 (4.08)
10a	0.389	**12a**	0.325	73.45 (74.40)	4.01 (4.21)	3.46 (3.65)
10b	0.372	**12b**	0.295	73.12 (74.20)	4.46 (4.24)	3.51 (3.68)

[a] Inherent viscosity determined in DMF at 25°C.
[b] Theoretical values of polyimides in parentheses.

out by sequential heating at 100, 200 and 250°C for 1 h each.

3.3. Polymer properties and effect of anions on properties of polymers

The solubility behaviour of polyimides based on bipyridinium is summarized in Table 2. For comparison, the solubility of bipyridinium-based polyimides with perchlorate and triflate as anions are also cited here. The polymers containing different anions displayed different solubility in organic solvents. Polyimides **11a** and **11b** were readily soluble in concentrated H_2SO_4, DMF, dimethyl acetamide (DMAc), DMSO and NMP. They also dissolved in hot *m*-cresol, pyridine (Py) and AN. Polyimides **12a** and **12b** dissolved well in concentrated H_2SO_4 as well as in hot DMF, DMAc, DMSO, NMP, *m*-cresol and Py. Obviously, the solubility of polymers containing different anions increased in the order: $CF_3SO_3^- > ClO_4^- > H_2PO_4^- > PTS^-$. This is also the order of increasing basicity of the anions. This indicates that the polymers bearing an anion with weaker basicity were more dissociated in solution and had better solubility.

The crystallinity of the polymers was examined by wide-angle X-ray diffraction (Fig. 4). **11b** revealed a slightly crystalline pattern, but **11a, 12a** and **12b** showed amorphous patterns.

Thermal characterization of the polymers was accomplished by d.s.c. and t.g.a. The thermal properties of the polyimides are summarized in Table 3. The glass transition temperatures (T_gs) of the polyimides containing $CF_3SO_3^-$ and PTS^- were found to be around 240°C and 300°C, respectively. T_gs of polyimides containing $H_2PO_4^-$ and ClO_4^- could not be observed until 400°C. The T_gs of the polyimides were obviously affected by the nature of the anions. The alkyl group of $-CH_3$ and $-CF_3$ in PTS^- and $CF_3SO_3^-$ along the backbone of polymers may act as a plasticizer. Polymers containing PTS^- have the lowest T_gs. This may be due to the fact that the bulk counterions disrupt the regularity of the polymer backbone. T.g.a. thermograms showed that 5% weight loss of **11** and **12** occurred between 410 and 390°C in nitrogen and between 419 and 402°C in air (Fig. 5). Polymers containing different anions exhibited an apparent difference in thermal stability. Their thermal stability increased in the order: $CF_3SO_3^- > H_2PO_4^- \sim PTS^- > ClO_4^-$ (Table 3). All of the bipyridinium-based polyimides displayed two decomposition processes in both air and nitrogen. Weight losses at the end of the first decomposition stage were consistent with the content of anions in the polymers. The polyimide

Table 2
Solubility of bipyridinium-based polyimides[a]

Polymer	Anion	Solvent[b]								
		Ac	AN	Py	DMF	DMAc	DMSO	NMP	*m*-Cresol	H_2SO_4
11a	$H_2PO_4^-$	–	+ –	+	+ +	+ +	+ +	+	+	+ +
11b	$H_2PO_4^-$	–	+	+	+ +	+ +	+ +	+	+	+ +
12a	PTS^-	–	–	+	+	+	+	+	+	+ +
12b	PTS^-	–	+ –	+	+	+	+	+	+	+ +
13a	ClO_4^-	–	–	+	+ +	+ +	+ +	+ +	+	+ +
13b	ClO_4^-	–	+ –	+	+ +	+ +	+ +	+ +	+	+ +
14a	$CF_3SO_3^-$	+ –	+	+ +	+ +	+ +	+ +	+ +	+	+ +
14b	$CF_3SO_3^-$	+ –	+ –	+ +	+ +	+ +	+ +	+ +	+	+ +

[a] Solubility: + +, soluble at room temperature; +, soluble in hot solvent; + –, partially soluble; –, insoluble.
[b] Ac, acetone; AN, acetonitrile; DMSO, dimethyl sulfoxide; DMF, *N*,*N*-dimethylformamide; DMAc, dimethyl acetamide; NMP, *N*-methylpyrrolidone; Py, pyridine.

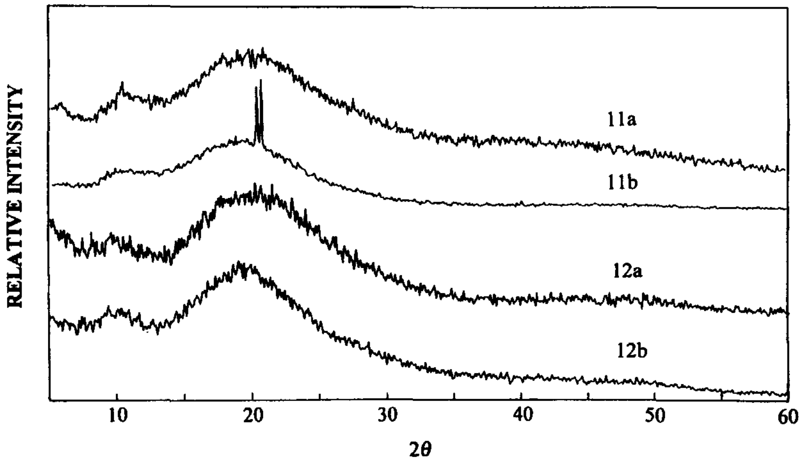


Fig. 4. Wide-angle X-ray diffractograms of polyimides **11a**, **11b**, **12a** and **12b**.

Table 3
Thermal behaviour data of bipyridinium-based polyimides

Polymer	Anion	T_g (°C)[a]	Decomposition temperature (°C)[b]		Content of anions (%)[c]	Weight loss (%)[d]
			In air	In nitrogen		
11a	$H_2PO_4^-$	—[e]	419	410	14.0	17
11b	$H_2PO_4^-$	—	401	390	14.1	18
12a	PTS^-	240	400	394	24.0	26
12b	PTS^-	243	402	391	24.0	26
13a	ClO_4^-	—	—	337	14.3	16
13b	ClO_4^-	—	—	344	14.4	15
14a	$CF_3SO_3^-$	302	477	468	20.0	23
14b	$CF_3SO_3^-$	296	488	471	20.2	22

[a] T_g was determined by d.s.c. at heating rate of 20°C min^{-1} under nitrogen.

[b] Temperature at which 5% weight loss was recorded by t.g.a. at a heating rate of 20°C min^{-1}.

[c] Weight per cent of anion in polymer.

[d] Weight loss at the end of the first decomposition stage.

[e] Could not be detected.

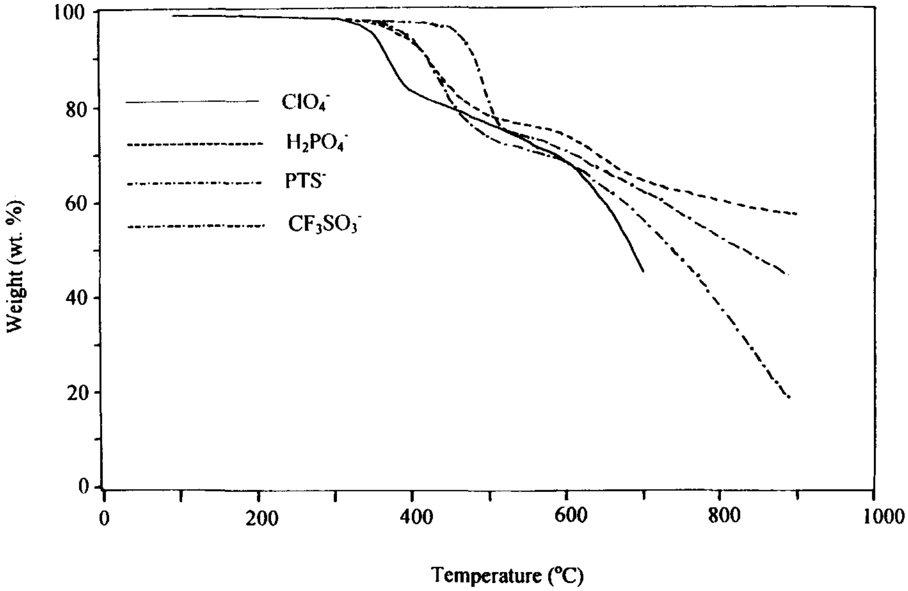


Fig. 5. T.g.a. thermogram of polyimides **11b**, **12b**, **13b** and **14b** bearing different anions.

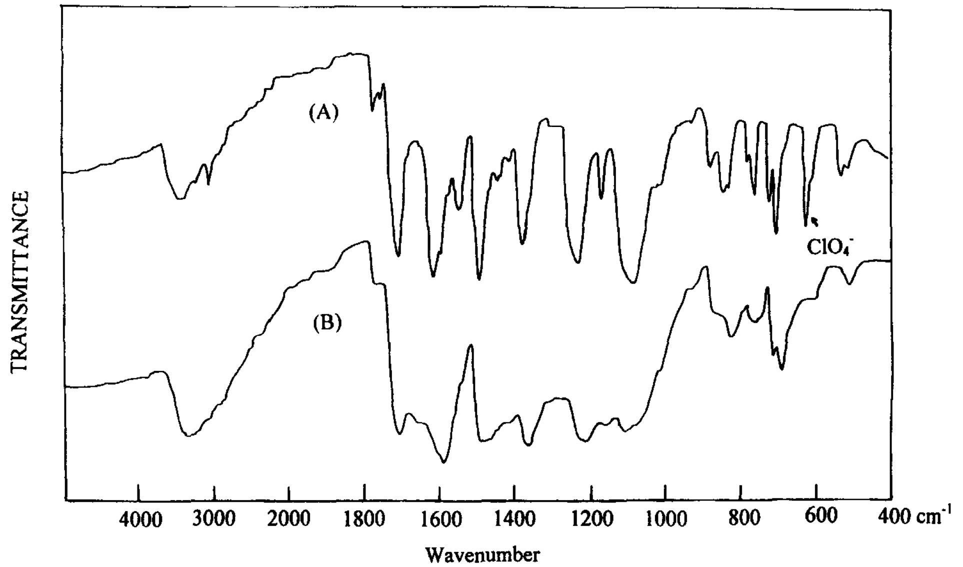


Fig. 6. I.r. spectra of polyimide **13b** before (A) and after (B) heating treatment at 350°C for 2 h.

13b was treated at 350°C for 2 h under nitrogen. The i.r. spectra showed that the absorption at 620 cm^{-1} due to ClO_4^- disappeared after the heat treatment (Fig. 6). These verified that the initial decomposition of these bipyridinium-based polyimides was decomposition of the anions. So, the thermal stability of these bipyridinium-based polyimides depends strongly on the thermal stability of their anions. Because the initial decomposition temperatures of the polymers in air were higher than those in nitrogen, it was postulated that decomposition of the anion involved an electron transfer from the anion to the bipyridinium cation. Generally speaking, this electron-transfer process could be hindered by oxygen.

Although all of the polymers show the same absorption bands at 310 and 262 nm in the u.v. region, see Fig. 7, changes in the anions could also have a drastic effect on visible light absorption (Table 4). The absorption of the polymers in the visible region was attributed mainly to a charge-transfer interaction between the counterion and the bipyridinium ring [28,29]. However, the hard/soft character of the counterion may be a useful consideration in understanding the optical density difference observed among the polymers [30]. The optical density of polymers increased in the order: $CF_3SO_3^- < ClO_4^- < PTS^- < H_2PO_4^-$, which is almost consistent with the decrease in hardness of the anions. The soft anion was more porlarizable and may be positioned closer to the bipyridinium nucleus, resulting in a higher intensity for the charge-transfer transition.

All of the polymers could be dispersed well in poly(vinyl pyrrolidone) (PVP) and films of them could develop colour reversibly under u.v. irradiation. All exhibited an absorption at 512 nm in the visible region after becoming coloured, but their photosensitivites were different in increasing order: $CF_3SO_3^- > H_2PO_4^- > PTS^- > ClO_4^-$ with changes of anions (Table 4).

4. Conclusions

Soluble polyimides containing bipyridinium dihydrogen phosphate and *p*-toluenesulfonate were synthesized to study the effect of anions on properties of the polyimides. Polymers containing anions with weaker basicity were more

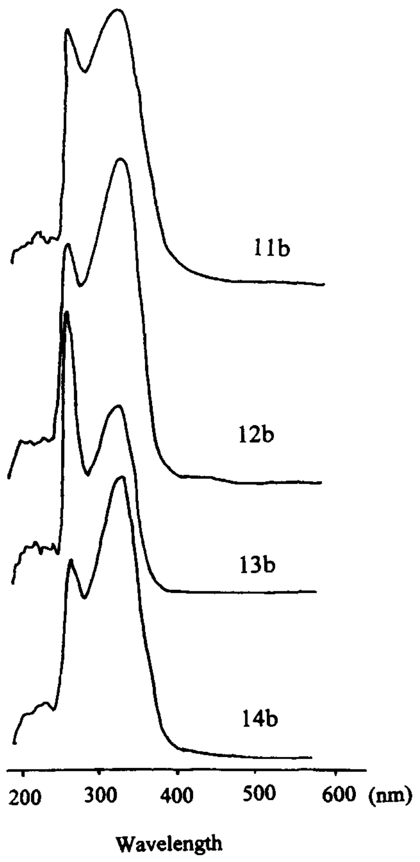


Fig. 7. U.v. absorption spectra for the polyimides bearing different anions in dilute DMF solution.

Table 4
Absorption spectral data of bipyridinium-based polyimides

Polymer	Anion	A_1 [a]	A_2 [b]
11b	$H_2PO_4^-$	9.6×10^{-3}	1.4×10^{-2}
12b	PTS^-	5.7×10^{-3}	1.3×10^{-2}
13b	ClO_4^-	2.8×10^{-3}	1.1×10^{-2}
14b	$CF_3SO_3^-$	1.4×10^{-3}	1.7×10^{-2}

[a] Polyimide films were employed as sample, A_1 = absorbance (500 nm)/film thickness (μm).

[b] After polyimide–PVP (1:4, wt/wt) films were irradiated by u.v. light for 3 min, A_2 = absorbance (512 nm)/film thickness (μm).

soluble in organic solvents. The T_gs of the polymers were also affected by the nature of the anions. For polymers containing $CF_3SO_3^-$ and PTS^-, T_gs were found around 240 and 300°C and for polymers containing $H_2PO_4^-$ and ClO_4^-, no T_g could be detected. The thermal stabilities of all polymers were determined by t.g.a. Thermograms showed that these polyimides underwent a two-step decomposition in both air and nitrogen. The first degradation occurred at lower temperature as a consequence of decomposition of the anions, whereas the second degradation of the main chain occurred at high temperature. So, the thermal stabilities of these polyimides were dependent on that of their anions, which increase in the order: $CF_3SO_3^- > H_2PO_4^- \sim PTS^- > ClO_4^-$. The visible light absorption of polymers was attributed to a charge-transfer interaction between the counterion and the bipyridinium ring. The optical density of the polymers increased with softness of the anions. All of these polyimides exhibited reversible photochromism and their photosensitivites were also different with change of the anions.

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