

Aromatic poly(pyridinium salt)s

Part 2. Synthesis and properties of organo-soluble, rigid-rod poly(pyridinium triflate)s[☆]

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Received 26 January 1999; received in revised form 1 July 1999; accepted 2 July 1999

Abstract

A bis[pyrylium tetrafluoromethanesulfonate (triflate)], i.e. *p*-bis[4-(2,6-diphenylpyrylium)]benzene dinitrate (**3**), has been prepared and polymerized with a series of aromatic diamines. The polymerizations, which were carried out in a dimethylsulfoxide (DMSO)/toluene mixture at 150°C for 3–4 h, were significantly faster than previous polymerizations of an analogous bis(pyrylium tetrafluoroborate). The poly(pyridinium triflate)s (**5**) obtained were soluble in polar aprotic solvents and had inherent viscosities that ranged from 8.3 to 18.7 dl/g (0.1 g/dl in DMSO at 30.0 ± 0.1°C). The rigid-rod polymers obtained from all-*para*-catenated diamines had viscosities comparable to those of other rigid-rod polyheterocyclics. All of the polymers could be solution cast into tough thin films that had moduli of 2.3–5.5 GPa. The poly(pyridinium triflate)s (**5**) were significantly more thermally and thermooxidatively stable than analogous poly(pyridinium tetrafluoroborate)s. The polymers underwent 5% weight losses near 451°C in nitrogen and near 461°C in air when subjected to thermal gravimetric analysis at a heating rate of 10°C/min. The differences in the poly(pyridinium salt) stabilities were shown to be due to the differences in the stabilities of the counter ions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Bis(pyrylium salt); Poly(pyridinium salts)s; Poly(pyridinium triflate)s

1. Introduction

Polymers containing quaternary nitrogen atoms in the backbone are referred to as ionenes [1]. The ionenes comprised of positively charged pyridine rings are generally referred to as aromatic ionenes, although they may also contain aliphatic units in the polymer backbone. Such aromatic ionenes are also known as poly(pyridinium salt)s. These materials, which belong to a class of polymers known as reduction–oxidation or redox polymers [2,3], have considerable potential for use in electron-exchange membranes [4] and as semiconducting materials [5]. Due to the positive charges located along their backbones, they also may be utilized as ionic conductors and in ion-exchange membranes.

Phenylated heterocyclic polymers are known for their solubility in organic solvents and film-forming ability [6–8]. All-aromatic polymers are recognized for their

thermal and chemical stability. Hence, it was postulated in this laboratory several years ago that all-aromatic, phenylated poly(pyridinium salts) would demonstrate good film-forming abilities and excellent thermal and chemical stabilities. In fact, because of the formal positive charges on the polymer backbones, it was postulated that phenylated, rigid-rod poly(pyridinium salt)s could be prepared that would be soluble in organic solvents. These hypotheses led to the synthesis of a series of phenylated, aromatic poly(pyridinium tetrafluoroborate)s [9–11], which were quite soluble in polar aprotic solvents. The polymers were subsequently doped with iodine and utilized as particles in anhydrous electrorheological suspensions [12]. The synthetic route used to produce the poly(pyridinium salt)s involved the synthesis of a bis(pyrylium salt), i.e. *p*-bis[4-(2,6-diphenylpyrylium)]benzene ditetrafluoroborate, which was then polymerized with aromatic diamines in dimethylsulfoxide (DMSO)/toluene and in *N,N*-dimethylformamide (DMF)/toluene mixtures at elevated temperatures. These ‘ring transformation polymerizations’ produced polymers with inherent viscosities of 0.8–4.9 dl/g (0.5 g/dl in DMF at 30°C). Although these values were considerably higher than those of other poly(pyridinium salt)s [13,14], they

[☆] Paper based on the PhD dissertation of S.A.X. Huang, The University of Akron, Akron, OH, USA, 1993.

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were much lower than those of other rigid-rod polymers, such as poly(*p*-phenylenebenzobisthiazole) (PBT) and poly(*p*-phenylenebenzobisoxazole) (PBO), which typically display inherent viscosities higher than 10 dl/g [15–18]. The polymers were also not as thermally stable as expected.

The major objectives of this research were to increase the molecular weights of the all-aromatic poly(pyridinium salt)s and to increase their thermal stability. The approach involved the replacement of the tetrafluoroborate counter ion in the bis(pyrylium salt) with the trifluoromethanesulfonate (triflate) anion. This anion is a weaker base than the tetrafluoroborate anion. Thus, its salts are more dissociated in solution. This was expected to enhance the reactivity of the monomer. The triflate anion is also known for its thermal stability [19]. Thus, it was postulated that poly(pyridinium triflate)s would be more thermally stable than poly(pyridinium tetrafluoroborate)s.

2. Experimental

2.1. Instrumentation

Infrared absorption measurements (KBr and thin films) were performed on a Beckman FT-2100 infrared spectrometer. Proton nuclear magnetic resonance ($^1\text{H-NMR}$) measurements were conducted at 200 MHz on a Varian Gemini-200 spectrometer using tetramethylsilane (TMS) as an internal standard. Melting points were measured on a Meltemp capillary melting-point apparatus and were uncorrected. Inherent viscosity measurements were made at $30.0 \pm 0.1^\circ\text{C}$ with a Cannon-Ubbelohde No. 100 viscometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. The purity of the bis(pyrylium salt) monomer was analyzed with a Varian 5000 Liquid Chromatograph equipped with a C_{18} reverse-phase column and a Varian UV-50 wavelength-adjustable detector. Acetonitrile was used as the eluent. Thermal analysis was performed on a DuPont 9900 Analyzer equipped with a 910 DSC cell and a 952 TGA cell using a heating rate of $10^\circ\text{C}/\text{min}$. The tensile moduli of the films were evaluated on a Seiko Thermal Mechanical Analyzer (Model TMA/SS 100) with a SSC5040 disk station. The wide angle X-ray diffraction photographs (WAXD patterns) were obtained with a Philips X-ray generator equipped with a Cu alpha beam source.

2.2. Reagents

Reagent grade solvents and reagents were used as received. All of the commercially available aromatic diamines used in the experiments were subjected to sublimation under reduced pressure to afford colorless powders prior to polymerization. 4,4'-Oxydianiline, i.e. 4-aminophenyl ether, 1,4-diaminobenzene and 3,3'-dimethylbenzidine were purchased from Aldrich Chemical

Company. Benzidine was purchased from Fluka Chemie AG.

2.3. $\alpha,\alpha,\alpha',\alpha'$ -Tetra(phenacyl)-*p*-xylene (2)

Terephthalaldehyde (20.0 g, 0.150 mol) and acetophenone (108.5 g, 0.900 mol) were mixed in 500 ml of 95% ethanol and heated at 65°C until the solution became homogeneous. KOH (21.0 g, 0.375 mol) in 22.5 ml water was then added dropwise over 30 min with vigorous stirring. A yellow bischalcone intermediate precipitated immediately. The heterogeneous reaction mixture was then heated at reflux for 4–5 h. The *p*-bischalcone, which redissolved, was treated with two additional equivalents of acetophenone. The yellow-brown tetraketone that precipitated was collected by filtration, and washed with ethanol to afford 82.0 g (96%) of crude product. The crude product was recrystallized from toluene to produce 79.5 g (92%) of colorless crystals: mp $205\text{--}206^\circ\text{C}$ (Lit. [11] mp $205\text{--}206^\circ\text{C}$); IR(KBr) 1683 cm^{-1} (C=O).

2.4. *p*-Bis[4-(2,6-diphenylpyrylium)]benzene ditriflate (3)

A suspension of triphenylmethanol (7.80 g, 0.030 mol) in acetic anhydride (87.5 ml) was stirred and maintained at $20\text{--}25^\circ\text{C}$ in a water bath, while trifluoromethanesulfonic acid (triflic acid) (50 wt% in distilled water) (6.88 g, 0.0375 mol) was added carefully and slowly. Compound 2 (7.23 g, 0.0125 mol) was then added to the reaction mixture. After stirring overnight, the yellow precipitate that formed was collected by filtration, washed with acetic anhydride, and dried at 110°C under reduced pressure to afford 8.85 g (99%) of a yellow powder: mp $> 350^\circ\text{C}$ (decomposition); IR (KBr) 1612, 1500, 1466, 1399, 1152, and 1028 cm^{-1} ; $^1\text{H NMR}$ (DMSO d_6) δ 7.5–9.1 (br. 24H, aromatic) and 9.44 ppm (s, 4H, 3,5-aromatic). Anal. Calcd. for $\text{C}_{42}\text{H}_{28}\text{F}_6\text{S}_2\text{O}_8$: C, 60.14; H, 3.36. Found: C, 60.22; H, 3.33.

2.5. $2',2'$ -Bis(trifluoromethyl)-4,4'-dinitrobiphenyl

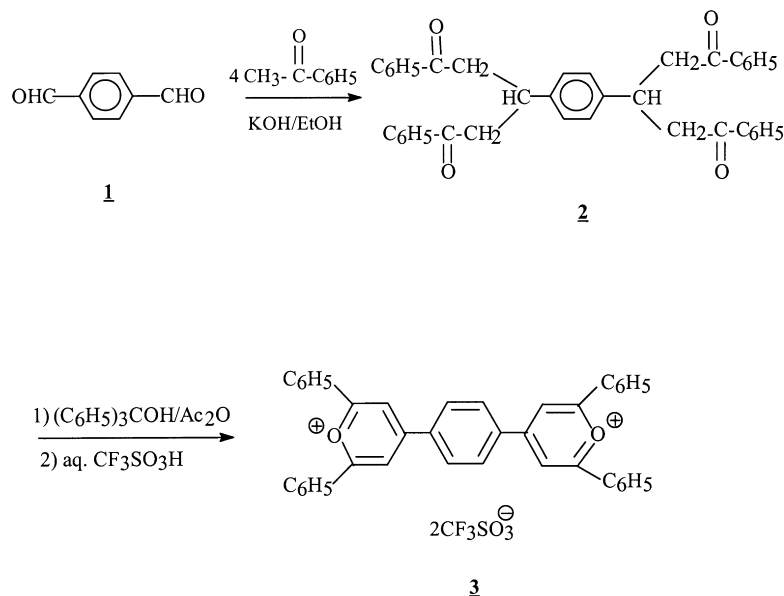
The dinitro intermediate was prepared from 2-bromo-5-nitrobenzotrifluoride by the known procedure [20]. The crude product was recrystallized from diethyl ether to afford yellow prisms in 71% yield: mp $138\text{--}140^\circ\text{C}$ (Lit. [20] mp $138\text{--}140^\circ\text{C}$).

2.6. $2,2'$ -Bis(trifluoromethyl)-4,4'-diaminobiphenyl

Reduction of the dinitro intermediate with stannous chloride in concentrated hydrochloric acid according to the known procedure [20] gave a white solid, which was recrystallized from a 1:1 (v/v) chloroform/hexane mixture to afford a 75% yield of short white needles: mp $180\text{--}182^\circ\text{C}$ (Lit. [20] mp $181\text{--}182^\circ\text{C}$).

2.7. Poly(pyridinium triflate)s (5)

A solution of *p*-bis[4-(2,6-diphenylpyrylium)]benzene



Scheme 1.

ditriflate (**3**) (40.00 mmol) and an aromatic diamine (40.00 mmol) in 240 ml of DMSO was heated at 110°C under nitrogen for 2 h. Toluene (100 ml) was then added so that the water generated could be removed by azeotropic distillation. The azeotrope and the excess toluene were gradually distilled from the reaction mixture at 150°C (bath temperature) using a Dean-Stark trap. The process was continued until the reaction mixture became gel-like and unstirrable, which took 4–5 h. The gel-like solution was diluted with DMSO (200 ml) and added slowly to a large excess of rapidly stirred diethyl ether. The yellow fibrous poly(pyridinium salt) that formed was collected by filtration, washed with ether, and dried at 120°C under reduced pressure overnight. The fibrous polymer was obtained in a quantitative yield: mp > 350°C (decomposition).

2.8. Determination of thin film mechanical properties

A 2 wt% solution of the poly(pyridinium salt) in DMSO was poured on a glass plate that was then heated at 80°C for 1 h and at 120°C for 12 h under reduced pressure. After being cooled to ambient temperature, the clear, tough film that formed was peeled from the plate and heated at 200°C for 10 h under reduced pressure to ensure the complete removal of the solvent. The dried film, which was about 0.03–0.08 mm thick, was cut into strips approximately 0.6 mm wide and 15 mm long. The mechanical properties of the films were determined on a Seiko Thermo Mechanical Analyzer (model TMA/SS 100) with an SSC5040 disk station using a strain rate of 0.05%/s (0.0127 mm/s).

2.9. Preparation of fibers

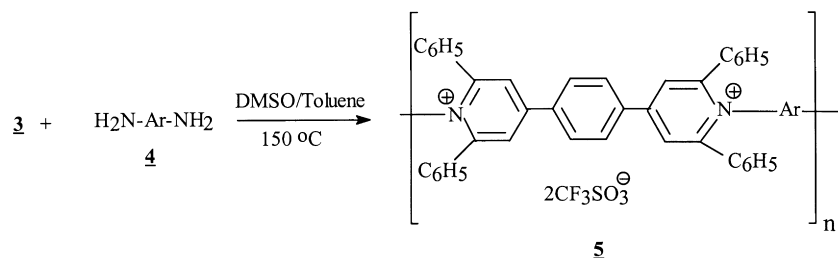
Fibers were obtained using a dry-jet, wet-spinning

process. The poly(pyridinium salt) dope (6 wt%), which was obtained directly from the polymerization solution, was heated in a bomb to 120°C. Pressure was then applied to the piston to force the dope through the spinneret. The piston movement was controlled by an Instron testing machine. The fibers were coagulated in an ethyl ether bath and then wound on a wheel. The speed of the wheel was controlled by a speed-adjustable motor. The fibers obtained were dried under reduced pressure at 110°C for 5 h.

3. Results and discussion

3.1. Monomer synthesis

A bis(pyrylium tetrafluoroborate) has been prepared previously in this laboratory by the cyclization of the tetraketone **2** with triphenylmethanol and fluoroboric acid [11]. The tetraketone was obtained by treating terephthalaldehyde with four equivalents of acetophenone in the presence of base. In order to obtain a monomer with triflate counter ions for this study, triflic acid was used in place of fluoroboric acid in the conversion of the tetraketone to the bis(pyrylium salt) (**3**). Since triflic acid is a very strong acid that can react very vigorously and cause side reactions, it was diluted with water to afford a 50 wt% aqueous solution before use. The FTIR spectrum of the bis(pyrylium triflate) **3**, which was obtained in quantitative yield, contained a C–F stretching band at 1270 cm⁻¹ due to the triflate counter ion. The ¹H-NMR spectrum of the pyrylium salt was very similar to that of the analogous bis(pyrylium tetrafluoroborate).



Scheme 2.

3.2. Synthesis of aromatic poly(pyridinium triflate)s

The bis(pyrylium triflate) **3** was polymerized with a series of aromatic diamines (**4**), using the procedure described previously [11,21] for the polymerization of a bis(pyrylium tetrafluoroborate) (Scheme 2). Thus, the triflate monomer was allowed to react with an aromatic diamine in DMSO at 110°C for 2 h. Toluene was then added and the mixture was heated to 150°C. At this point, the toluene/water azeotrope was allowed to distil into a Dean-Stark trap. In the previous

polymerizations of the tetrafluoroborate monomer, the distillation of the azeotrope was carried out for 10–16 h. However, in the reactions of the triflate monomer with the diamines, the polymerization mixtures became extremely viscous after the distillation of the azeotrope had proceeded for only 3–4 h. The viscosity continued to increase until the mixtures became gel-like and unstirrable. However, the gel-like masses could be broken up in excess DMSO to form clear, homogeneous, yellow solutions. The inherent viscosities of the poly(pyridinium triflate)s **5a–e** ranged from 8.3

Table 1
Properties of poly(pyridinium triflate)s

No	–Ar–	η_{inh}^a (dl/g)	Concentration ^b (g/dl)	¹ H NMR ^c			Tensile modulus ^d (GPa)
				6.4–7.1	6.8–8.0	7.9–9.0	
5a		8.3	0.12	4H	24H	8H	2.7
5b		18.7	0.11		28H	8H	5.5
5c		14.3	0.14	6H	28H	6H ^e	5.2
5d		11.3	0.14		28H	6H	2.3
5e		8.6	0.15		24H	8H	2.6

^a Inherent viscosity determined in DMSO at 30.0 ± 0.1°C with a concentration as indicated.

^b Concentration at which the inherent viscosity was measured.

^c Chemical shift (ppm) ranges for the aromatic hydrogens.

^d Determined on thin films.

^e ¹H-NMR spectrum also contained aliphatic absorptions (6H) at 1.7–2.2 ppm.

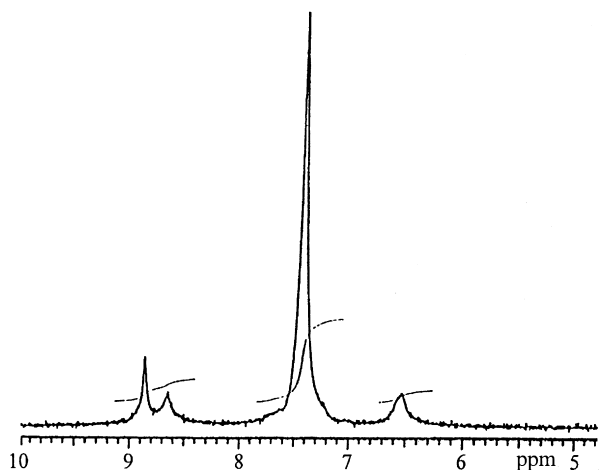


Fig. 1. $^1\text{H-NMR}$ spectrum of the poly(pyridinium triflate) **5a**.

to 18.7 dl/g (Table 1). The polymer solutions were so viscous that the inherent viscosities were determined at concentrations in the range of 0.11–0.15 g/dl, instead of at the standard concentration of 0.5 g/dl. Higher concentrations resulted in inordinately long flow times. The inherent and reduced viscosities both increased dramatically when the polymer concentrations were reduced below 0.1 g/dl [22]. The polyelectrolyte effect will be described in detail in a future publication.

The dramatic differences in the reactivities of the bis(pyrylium tetrafluoroborate) and bis(pyrylium triflate) monomers can be attributed to the different counter ions. Triflic acid is a stronger acid than tetrafluoroboric acid (HBF_4) [23,24]. Its dissociation constant (K_{diss}) in trifluoroacetic acid is $10^{-3.8}$, while the K_{diss} of HBF_4 in glacial acetic acid is $10^{-5.2}$. Therefore, the triflate anion is a weaker base than the tetrafluoroborate anion. Elshafie treated 2,4,6-triphenylpyrylium salts containing different counter ions with butyl amine to determine the effects of the counter ion on the reaction rate [25]. The rate constants for these reactions varied by over a factor of 15 and decreased as the counter ion was changed in following order: $\text{IO}_4^- > \text{BF}_4^- > \text{ClO}_4^- > \text{IO}_3^- > \text{I}^- > \text{Cl}^- > \text{Br}^-$. The differences in rate constants were attributed to the differences in ion pair association. This was reflected in this work in that the polymerizations of the triflate salt with the aromatic diamines proceeded much faster (3–4 h) than those with the analogous tetrafluoroborate salt (10–16 h). The polymerizations of the bis(pyrylium triflate) also afforded polymers with inherent viscosities as high as 18.7 dl/g (Table 1), while the highest viscosity displayed by a poly(pyridinium tetrafluoroborate) prepared from a tetrafluoroborate salt was only 4.9 dl/g.

The most flexible polymer (**5a**), which was obtained from 4,4'-oxydianiline, displayed the lowest inherent viscosity probably because the flexible ether linkage resulted in less chain extension in solution. Polymers **5b–e** are all true rigid-rods. The polymer (**5b**) made from benzidine had the

highest inherent viscosity. The inherent viscosity of the polymer (**5c**) produced from 3,3'-dimethylbenzidine was slightly less. The steric hindrance due to the methyl groups may have slightly hampered the polymerization. The inherent viscosity of the polymer (**5d**) obtained from 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl was less than that of **5c**. In this case, the monomer is known to be less reactive due to the electron-withdrawing trifluoromethyl groups. The polymer was also light yellow, while the other polymers were darker yellow. This can be attributed to the substituents at the 2- and 2'-positions in the biphenyl moiety, which prevent the rings from assuming a planar conformation and, thus, disrupt the conjugation along the backbone [20].

Poly(pyridinium salt)s obtained previously from bis(pyrylium salt) monomers and 1,4-diaminobenzene had low inherent viscosities. For example, a polymer with an inherent viscosity of only 0.8 dl/g was obtained from a bis(pyrylium tetrafluoroborate) and 1,4-diaminobenzene [11]. In this study, although the polymer (**5e**) prepared from the bis(pyrylium triflate) monomer and 1,4-diaminobenzene had a much higher inherent viscosity (8.3 dl/g), it was lower than those of the other rigid-rod poly(pyridinium triflate)s. The lower molecular weights can be attributed to both electronic and steric effects. After the first amino group in the diamine reacts, the positively-charged pyridinium ring functions as a strong electron-withdrawing group, which makes the second amino group much less reactive. The reaction of the second amino group is also sterically hindered.

3.3. Spectroscopic analysis of the poly(pyridinium triflate)s

The $^1\text{H-NMR}$ spectra of polymers **5a–e** in DMSO-d_6 contained broad aromatic absorptions between 7.0 and 8.0 ppm and pyridinium ring absorptions between 8.0 and 9.0 ppm (Table 1). The largest chemical shifts were assigned to the protons located closest to the positively charged nitrogens. A typical spectrum is shown in Fig. 1. According to the proposed mechanism for the conversion of the pyrylium salt to pyridinium salt [26,27], the last ring-closure step involves a nucleophilic attack of a vinylogous amino group on a carbonyl group, followed by the loss of a water molecule. The FTIR spectra did not contain any absorptions that could be attributed to olefinic protons. The spectra contained a strong aromatic stretch band at 1620 cm^{-1} , a C–N stretch band at 1490 cm^{-1} , and a C–F stretch band at 1270 cm^{-1} . The $^{13}\text{C-NMR}$ spectra contained aromatic carbon absorptions between 120 and 160 ppm. A carbonyl absorption at 186 ppm, previously attributed to a vinylogous amine structure [26], was not present. Thus, no incomplete ring closures could be detected with these spectroscopic techniques.

3.4. Thermal analysis of the poly(pyridinium triflate)s

Differential scanning calorimetry (DSC) was used in an

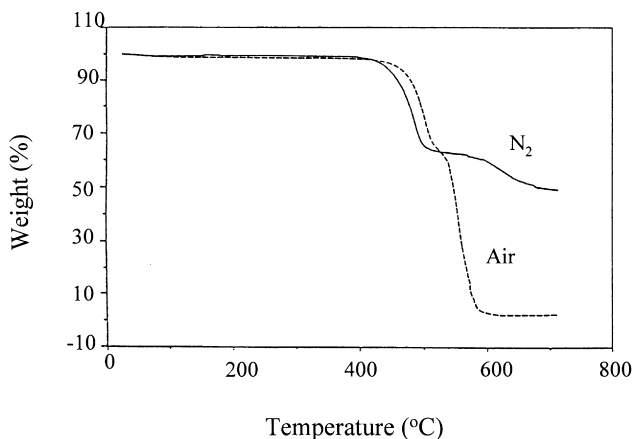


Fig. 2. TGA thermograms for the poly(pyridinium triflate) **5b** obtained with a heating rate of 10°C/min.

attempt to determine the transition temperatures. Despite repeated runs, no glass transition temperatures (T_g s) could be detected with DSC below 400°C. However, transitions below this temperature cannot be ruled out because aromatic polyheterocyclics often undergo very small changes in heat capacity at the T_g . Although wide-angle X-ray diffraction (WAXD) analysis indicated a low degree of crystallinity, no melting endotherms could be detected below 400°C. Evidently, the polymers decomposed prior to melting.

The poly(pyridinium triflate)s, which had higher thermal and thermo-oxidative stabilities than those of analogous poly(pyridinium tetrafluoroborate)s, underwent 5% weight losses in the range of 450–452°C in nitrogen and in the range of 460–462°C in air when subjected to thermal gravimetric analysis (TGA) with a heating rate of 10°C/min (Fig. 2). The higher stabilities of the poly(pyridinium triflate)s suggest that the stability of a poly(pyridinium salt) is primarily determined by its counter ion. As stated

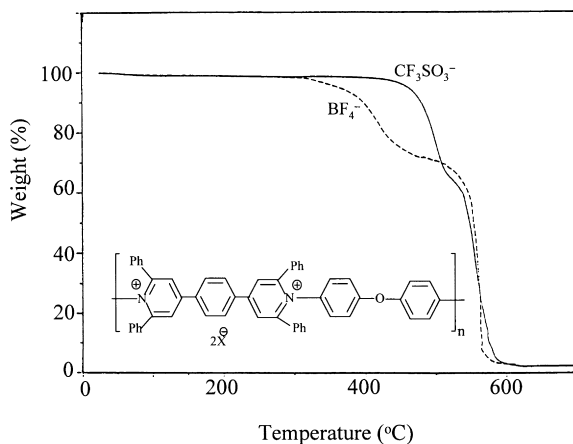


Fig. 3. TGA thermograms for the poly(pyridinium triflate) **5a** and a poly(pyridinium tetrafluoroborate) obtained in air with a heating rate of 10°C/min.

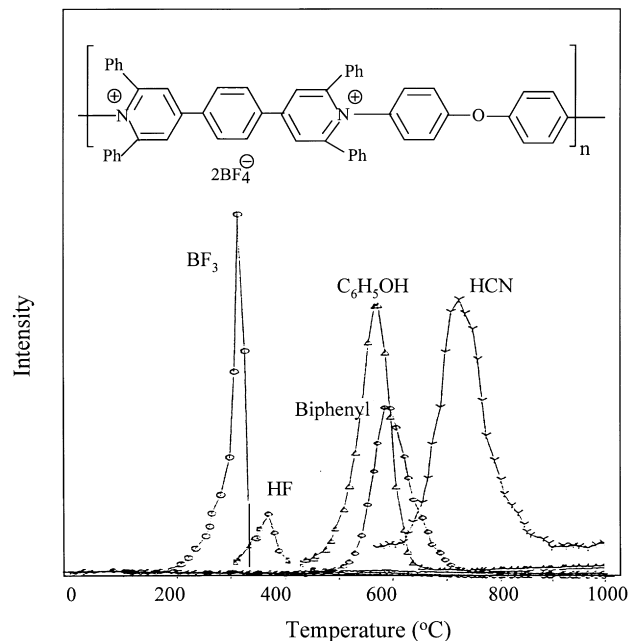


Fig. 4. TGA/mass spectrometry of a poly(pyridinium tetrafluoroborate).

earlier, the triflate anion is known for its thermal stability [19]. In fact, it appears to be slightly more stable in air than in nitrogen. This would suggest that oxygen interferes with the decomposition process, which could involve an electron transfer from the anion to a pyridinium ring [28,29]. The thermooxidative stabilities of a poly(pyridinium triflate) and an analogous poly(pyridinium tetrafluoroborate) are compared in Fig. 3. As shown in the figure, the temperature of which the triflate underwent a 5% weight loss was approximately 100°C higher than the temperature where the same weight loss occurred with the poly(pyridinium tetrafluoroborate). Both polymers underwent decomposition in two stages. In each case, the weight loss in the first stage was proportional to the weight fraction of the counter ion.

The thermal decomposition of polymers **5b** and a poly(pyridinium tetrafluoroborate) was studied further by TGA/mass spectrometry at the US Air Force Systems Research Laboratory in Dayton, Ohio. In the case of tetrafluoroborate polymer, the initial decomposition products were identified as boron trifluoride (BF_3) and hydrofluoric acid (HF), which can be attributed to the decomposition of the tetrafluoroborate (BF_4^-) counter ion (Fig. 4). Evidently, the aromatic rings in the backbone decomposed to form phenol and biphenyl above 500°C. The pyridinium rings decomposed last to form hydrocyanic acid (HCN) at 700°C. The triflate polymer **5b** underwent initial decomposition at 450°C to produce sulfur dioxide (SO_2) and trifluoromethane (CF_3H) (Fig. 5). Thus, the counter ion in this polymer also decomposed before the backbone. The pattern of the backbone decomposition was similar to that of the tetrafluoroborate polymer. The results suggest that the triflate counter ion is stable to a temperature approximately

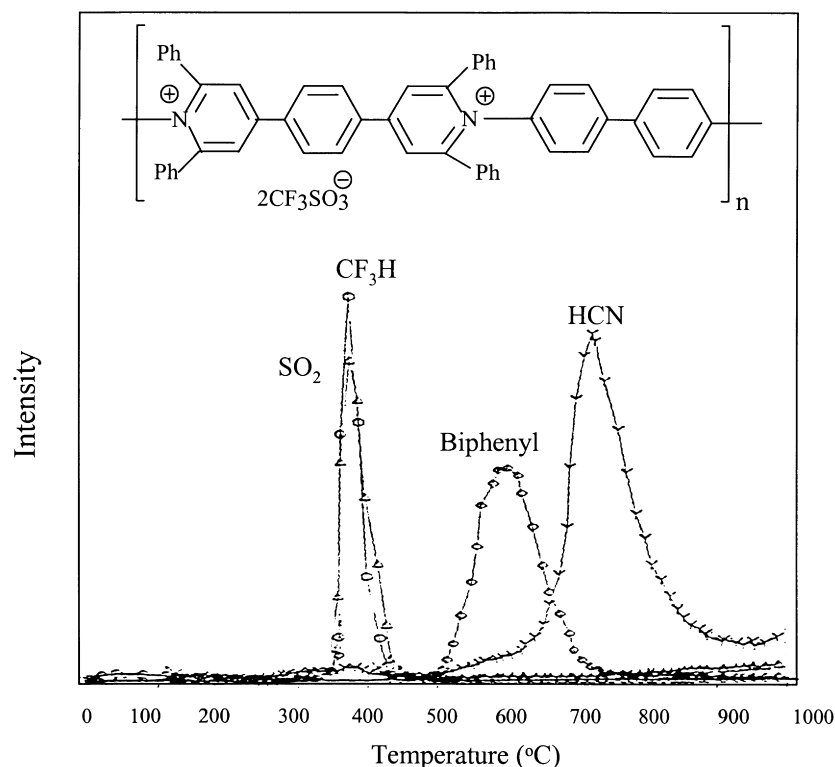


Fig. 5. TGA/mass spectrometry of the poly(pyridinium triflate) **5b**.

100°C higher than the temperature where the tetrafluoroborate ion decomposes. A study on polyimides containing bis(pyridinium triflate)s conducted subsequent to this work showed that the triflate counter ion is also considerably more stable than the perchlorate counter ion [30].

3.5. Mechanical properties of aromatic poly(pyridinium triflate) films

The light yellow, fibrous polymers were soluble in

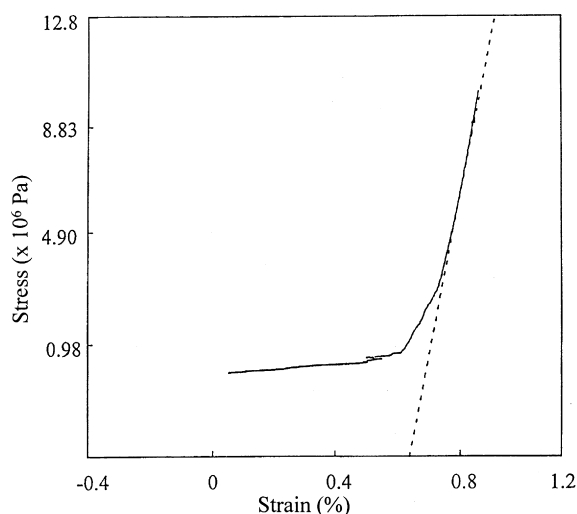


Fig. 6. Stress–strain curve for a thin film of poly(pyridinium triflate) **5c**.

polar organic solvents, such as DMSO, DMF, DMAc, etc. The excellent solubility of these rigid aromatic polymers can be attributed to their pendant phenyl groups and to the positive charges located along their backbones. Clear, yellow, flexible films were cast from DMSO solutions. The films were ‘fingernail creasable’, which indicates a somewhat surprising degree of toughness.

Stress-vs.-strain measurements were carried out on thin films of the polymers. Although the film tensile strengths were only approximately 10 MPa, the moduli were quite high. The moduli of films of **5b** and **5c** were the highest, with values of 5.5 and 5.2 GPa, respectively (Table 1). The film elongations were approximately 1%. The stress–strain curve of polymer **5c** is shown in Fig. 6. The high moduli of these aromatic poly(pyridinium salt)s is a reflection of their rigid-rod nature and the ionic interaction in the solid state.

3.6. Poly(pyridinium triflate) fibers

Dilute solutions of the high molecular weight poly(pyridinium triflate)s in DMSO were extremely viscous. In fact, a non-stirrable, gel-like state formed at a concentration of approximately 5 wt%. Fibers of **5a** and **5b** were spun from such dilute solutions using a dry-jet, wet-spinning process. When the fibers were examined through a polarized, optical microscope, a strong birefringence was observed, indicating structural anisotropy. Although the WAXD pattern of this fiber revealed some crystallinity, the chains were not

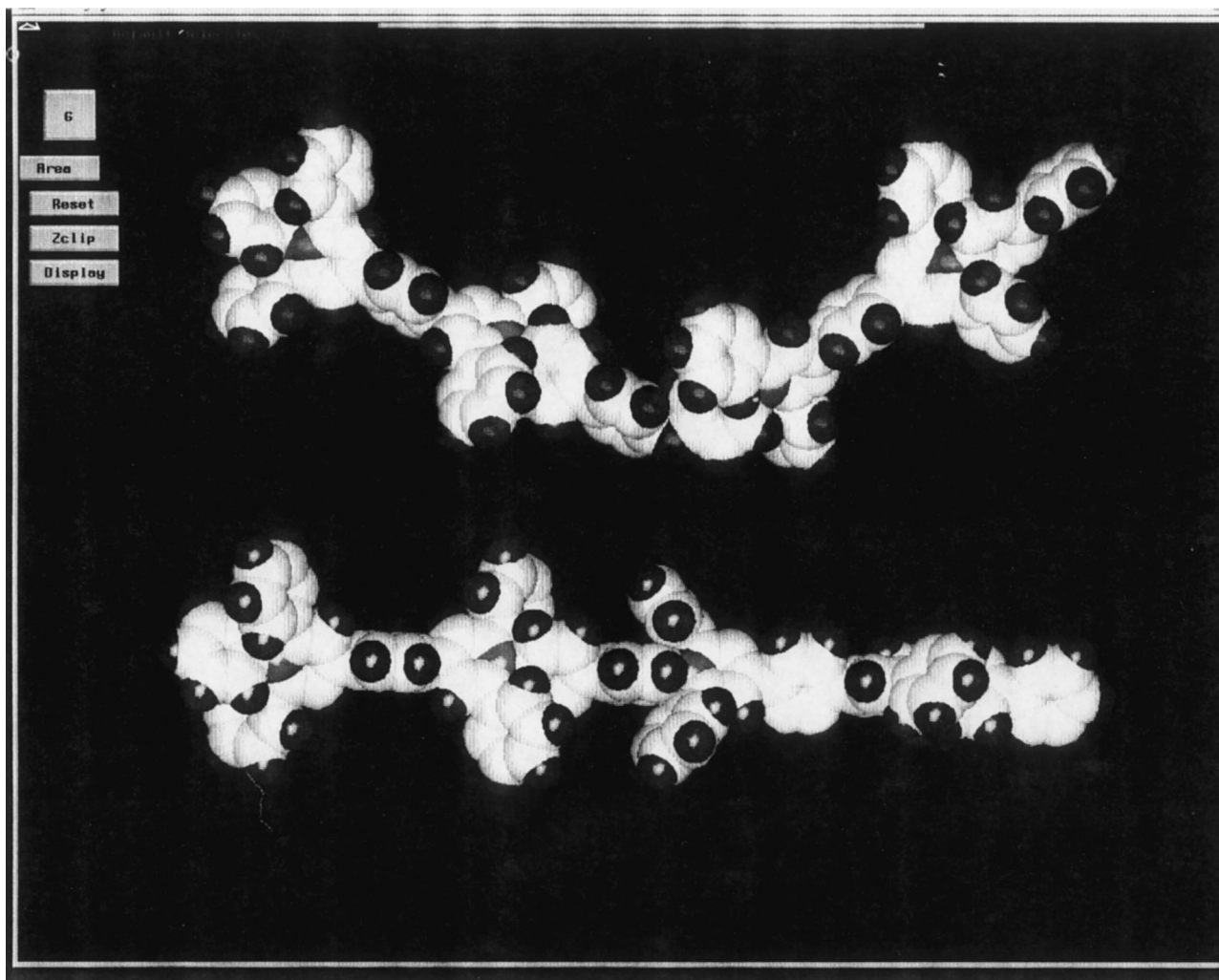


Fig. 7. Molecular models of pyridinium triflate dimers.

oriented. An attempt was made to draw the fibers at elevated temperature to induce orientation. Unfortunately, the fibers were too brittle and could not be drawn further.

3.7. Molecular modeling

As stated earlier, polymers **5b–e** are rigid-rod molecules, i.e. their backbones consist of *para*-catenated aromatic rings that can only rotate around the axis of the backbones. Polymer **5a** is not a rigid-rod molecule because the oxygen atoms in the backbone result in kinked linkages. To better visualize the polymer structures, molecular models of the minimized energy conformations [22] of dimer segments of polymers **5a** and **5b** were prepared using local energy minimization on a Silicon Graphics 220GTX workstation equipped with Tripos Associates Sybyl software (version 5.2) (Fig. 7). The model of the **5b** dimer clearly shows that the molecule is a true rigid-rod with the two central aromatic rings twisted about 15° along its axis to minimize the potential energy. The backbone of the **5a** dimer is also clearly not linear.

A molecular model of a dimer segment of polymer **5e**, which only has one benzene ring between the phenylated pyridinium salt moieties, was also prepared. The model was examined to determine if there was any steric hindrance between the phenyl substituents on the pyridinium rings attached to the same benzene ring. In this case, the two adjacent pyridinium salt units are twisted about 90° from the central benzene ring to minimize the potential energy. Therefore, it is likely that there is some steric hindrance to polymerization.

4. Conclusions

p-Bis[4-(2,6-diphenylpyrylium)]benzene ditriflate (**3**) is considerably more reactive than *p*-bis[4-(2,6-diphenylpyrylium)]benzene ditetrafluoroborate). The triflate salt rapidly undergoes polymerization with aromatic diamines at 150°C in DMSO to afford high molecular weight poly(pyridinium triflate)s. The ring transformation polymerizations with all-*para*-catenated diamines afford

organo-soluble, rigid-rod polymers with inherent viscosities as high as 18.7 dl/g. The polymers can be solution cast into tough, thin films with tensile moduli as high as 5.5 GPa. The poly(pyridinium triflate)s are significantly more thermally and thermooxidatively stable than analogous poly(pyridinium tetrafluoroborate)s. This can be attributed to the fact that the triflate counter ion is considerably more stable than the tetrafluoroborate counter ion.

Acknowledgements

The financial support of a portion of this work by Ballard Advanced Materials is gratefully acknowledged. The authors would also like to thank Professors Z. Wu and D. Shen for the fiber spinning studies; Fred Arnold, Jr. and the US Air Force Systems Research Laboratory for the TGA/Mass spectrometry work; and Professor A. Zhang for the X-ray diffraction measurements.

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