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Polymer 43 (2002) 3421–3430

polymer

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Aromatic poly(pyridinium salt)s. Part 3. Photoreduction in amide solvents

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Dedicated to Professor Imanishi on the occasion of his retirement

Received 25 December 2001; received in revised form 12 February 2002; accepted 13 February 2002

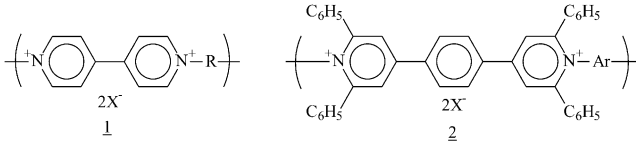
Abstract

UV–Vis irradiation of bis(pyridinium salt) model compounds and poly(pyridinium salt)s in amide solvents result in dramatic changes in their UV–Vis spectra. The absorption maximum near 342 nm, characteristic of pyridinium rings, disappears, while an absorption maximum near 500 nm appears and then disappears. During this process, the solutions change from yellow to dark red to light yellow. The inherent viscosities of the poly(pyridinium salt)s also decrease dramatically under UV–Vis irradiation. Both the color changes and the viscosity decreases are unaffected by the nature of the pyridinium salt counter anion. However, they are dramatically affected by the presence of pendent substituents. Electron-withdrawing groups increase the rate at which these changes take place, while electron-donating groups retard them. It is speculated that the photodecomposition proceeds through the initial formation of radical cations. It is also speculated that the amide groups may serve as reducing agents providing electrons in the electron transfer process. Evidence for this comes from the fact that a poly(pyridinium salt) containing pendent amide groups underwent photoreduction in DMSO in marked contrast to other poly(pyridinium salt)s that are photostable in this solvent. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(pyridinium salt)s; Photoreduction; Photodecomposition

1. Introduction

The most well-known examples of poly(pyridinium salt)s are the polyviologens (**1**), which contain 4,4′-bipyridinium salt moieties (viologen units) separated by alkyl or alkylaryl spacers [1–6]. These polymers are usually formed by the Menschutkin reaction of 4,4′-dipyridine with dihaloalkanes or dihaloarylalkanes. Because viologens have one of the lowest cathodic redox potentials known for any organic compound, they are easily reduced to highly colored radical cation salts [7]. The radical cations readily undergo oxidation in solution or in the solid state to regenerate the starting materials. However, their use in most applications is prevented by their poor mechanical properties, which result from their low molecular weights ($\bar{M}_n \sim 10\,000$). Several approaches have been used to overcome this problem. For example, they have been complexed with poly(styrene sulfonate) in the preparation of modified electrodes [2–4]. Viologen units have been incorporated in copolymer backbones [8–10] and attached to polymer backbones as pendant substituents [11–16]. Low molecular weight viologens have also been embedded in polymer matrices [17–19]. Polyviologen systems have been found to display photochromism [9,16,17,19], electrochromism [14], thermochromism [5] and photomechanical behavior [10].



A new class of poly(pyridinium salt)s (**2**) is under development in our laboratory [20,21]. In these polymers, two *N*-aryl pyridinium salt moieties are separated by a 1,4-phenylene unit. The pyridinium rings also contain phenyl substituents in the 2- and 6-positions. The polymers are prepared by the polymerization of bis(pyrylium salt)s with aromatic diamines in *N*,*N*-dimethylformamide (DMF) or dimethylsulfoxide (DMSO) at elevated temperatures. The highest molecular weight products are obtained in DMSO. In fact, poly(pyridinium triflate)s with inherent viscosities as high as 18.7 dl/g have been obtained in this solvent [21]. The polymers are not soluble in water but are soluble in polar aprotic organic solvents and organic acids. Recently, poly(pyridinium tosylate)s have been found to display

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PII: S0032-3861(02)00148-9

lyotropic properties in methanol and DMSO [22]. Poly(pyridinium salt)s can be solution cast into thin films that display excellent properties. Thus, they are easier to fabricate into devices than polyviologens. Iodine-doped powders of these materials have been used in electrorheological fluids [23].

During a recent study aimed at determining the effects of the pyridinium salt counter ion on the polymer properties, several unusual, previously unnoticed phenomena were observed [24]. Dilute DMF solutions of the poly(pyridinium salt)s changed from yellow to red or deep red upon storage at room temperature on a lab bench for several hours. When the viscosities of the polymers were measured in DMF, the data were not reproducible. The viscosity appeared to be decreasing during the measurement. As these phenomena were examined more closely, it became clear that they were related to light irradiation. The objective of this work was to investigate this photobehavior.

2. Experimental

2.1. Instrumentation

Proton and carbon nuclear magnetic resonance (^{1}H NMR) spectra were measured at 200 MHz on a Varian Gemini-200 spectrometer. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN. All melting points were determined on a Mel-Temp melting point apparatus and were uncorrected. Inherent viscosities were determined with Cannon-Ubbelohde No. 100 viscometers. Flow times were recorded for *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), formic acid (FA), and methylsulfoxide (DMSO) solutions with different polymer concentrations at 30 ± 0.1 °C. Thermogravimetric analyses (TGA) were obtained in nitrogen and air with a TA Hi-Res TGA 2950 thermogravimetric analyzer using a heating rate of 10 °C/min. DSC results were recorded in nitrogen with a DuPont 910 differential scanning calorimeter.

All UV–Vis absorption measurements were performed on a Hewlett Packard model 8451A Diode Array Spectrophotometer. Wavelengths were generally scanned from 200 to 820 nm, with resolution of ±2 nm, and slits fixed at 2 nm. Solutions were prepared (10 μg/ml) in vials and diluted, if necessary, to attain the desired optical density range of 0.05–1.0 AU (absorbance unit).

A Blak-Ray UVP High Intensity Longwave Lamp (B-100Ap Model) was used as a UV irradiation source. Solution samples for UV–Vis measurement were irradiated at a distance of 20 cm in a quartz cuvet. Solution samples (0.2 g/dl) for viscosity measurements were irradiated at a distance of 30 cm in a Cannon-Ubbelohde No. 100 viscometer. The film samples of poly(pyridinium salt) **14** were irradiated directly at a distance of 20 cm.

2.2. Monomer syntheses

2.2.1. 3,3′-(p-Phenylene)bis(1,5-diphenyl-1,5-pentanedione) (**3**)

Terephthalaldehyde (20.0 g, 0.150 mol) and acetophenone (108.5 g, 0.900 mol) were added to 500 ml of 95% ethanol in a 1000-ml three-neck flask. The mixture was heated at 55–65 °C until the terephthalaldehyde totally dissolved. To the solution, potassium hydroxide (21.0 g, 0.375 mol) in 21 ml of water was added dropwise over 30 min with mechanical stirring. During the addition of potassium hydroxide, the temperature of the system was maintained below 65 °C. A yellow bischalcone precipitated immediately. The resulting heterogeneous mixture was then heated at reflux for an additional 5 h. The product was collected by filtration and washed with ethanol. The crude product was recrystallized from toluene to afford 78.0 g (90%) of light yellow needles: mp 206–208 °C (Ref. [25,26] mp 205 °C); ^{1}H NMR (d-DMSO) δ 3.35 (t, 8H, C–H), 4.00 (m, 2H, C–H), 7.20 (s, 4H, Ar-H), 7.45 (m, 12H, Ar-H), and 8.90 ppm (d, 8H, Ar-H).

2.2.2. 4,4′-(p-Phenylene)bis(2,6-diphenylpyrylium perchlorate) (**4a**)

A suspension of triphenylmethanol (5.20 g, 0.020 mol) in acetic acid (75.0 ml) was added to a 300-ml three-neck round-bottom flask equipped with a mechanical stirrer. After the mixture was heated to 60 ± 5 °C until the triphenylmethanol totally dissolved, it was cooled to between 20 and 25 °C. To the cloudy solution, 5.02 g (0.025 mol) of a 50 wt% perchloric acid aqueous solution was added dropwise. The solution slowly became homogeneous during the addition. The solution was maintained between 20 and 25 °C with a water bath. After 4.82 g (0.008 mol) of solid 3,3′-(*p*-phenylene)bis(1,5-diphenyl-1,5-pentanedione) was added portionwise, the mixture was heated to 100 ± 5 °C and maintained at that temperature for 3 h. During this time, an orange powder precipitated from the solution. The mixture was filtered while it was hot. The orange powder was collected and washed with acetic acid. The product was dried at 110 °C under reduced pressure to afford 5.50 g (90.0%) of an orange powder: mp > 300 °C (Ref. [25,26] no mp reported); ^{1}H NMR (d-DMSO) δ 7.50–8.20 (br., 16H, Ar-H), 8.50–8.80 (br., 8H, Ar-H) and 9.35 ppm (s, 4H, H on pyrylium ring).

2.2.3. 4,4′-(p-Phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) (**4b**)

The same procedure was used to synthesize this compound as used for **4a**. In this case, tetrafluoroboric acid was used in place of perchloric acid. The final product was dried under reduced pressure to afford a yellow powder in 95.0% yield: mp 350 °C (decomposition) (Ref. [27,28] mp 350 °C); ^{1}H NMR (d-DMSO) δ 7.50–8.20 (br., 16H, Ar-H), 8.50–8.80 (br., 8H, Ar-H), and 9.35 ppm (s, 4H, H on pyrylium ring).

*2.2.4. 4,4′-(p-Phenylene)bis(2,6-diphenylpyrylium triflate) (**4c**)*

A suspension of triphenylmethanol (5.20 g, 0.020 mol) in acetic anhydride (60.0 ml) was stirred and maintained at 20–25 °C in a water bath, while a 50 wt% trifluoromethanesulfonic acid (triflic acid) aqueous solution (3.75 g, 0.025 mol) was added slowly. The solution was stirred for another 1 h at 20–25 °C. 3,3′-(*p*-Phenylene)-bis(1,5-diphenyl-1,5-pentanedione) (**3**) (4.83 g, 0.008 mol) was then added to the reaction mixture. After stirring overnight, the yellow precipitate that formed was collected by filtration and washed with acetic anhydride to afford 6.50 g (93.3%) of a yellow powder: mp > 350 °C (decomposition) [21].

*2.2.5. 4,4′-Dinitrodiphenic acid (**11**)*

Diphenic acid (20.0 g, 0.083 mol) was dissolved in sulfuric acid (650 ml), and the solution was cooled to 0 °C. Nitric acid (20 ml) was added dropwise, while the solution was maintained below 5 °C. The solution was stirred at room temperature overnight and then poured into ice water (1000 ml). The precipitate that formed was collected by filtration and recrystallized from a 30% ethanol/water mixture to yield 19.68 g (71%) of yellow crystals: mp 257–259 °C (Ref. [29] mp 258–259 °C).

2.2.6. 4,4′-Dinitro-2,2′-biphenoyl chloride

4,4′-Dinitrodiphenic acid (20.0 g, 0.060 mol) was heated at 70 °C with a 20-fold excess of thionyl chloride in a single-neck flask for 3 h. A small amount of pyridine was added to the mixture to neutralize the hydrogen chloride generated during the reaction. The excess thionyl chloride was removed by distillation under reduced pressure. The residue was recrystallized twice from benzene to give 12.0 g (54.2%) of white crystals: mp 129–132 °C; ^{1}H NMR (d-DMSO) δ 7.53 (d, 2H, Ar-H), 8.45 (d, 2H, Ar-H) and 8.68 ppm (s, 2H, Ar-H).

*2.2.7. 4,4′-Dinitro-2,2′-bis(N,N′-diethylcarbamoyl)-biphenyl (**12**)*

After 4,4′-dinitro-2,2′-biphenoyl chloride (7.38 g, 0.020 mol) was dissolved in 75.0 ml of methylene chloride, diethylamine (4.32 g, 0.060 mol) was added. The solution was stirred for 2 h at room temperature. After the methylene chloride was removed on a rotovapor, the residue was recrystallized from ethanol/water (2:1) to afford 7.50 g (84.7%) of a white powder: mp 210–212 °C; ^{1}H NMR (d-DMSO) δ 3.30 (m, 12H, C–H), 4.34 (m, 8H, C–H), 7.55 (d, 2H, Ar-H), 8.21 (s, 2H, Ar-H) and 8.30 ppm (d, 2H, Ar-H). Anal. calcd for $C_{22}H_{26}N_4O_6$: C, 59.72%; H, 5.92%; N, 12.66%. Found: C, 59.54%; H, 6.06%; N, 12.54%.

*2.2.8. 4,4′-Diamino-2,2′-bis(N,N′-diethylcarbamoyl)-biphenyl (**13**)*

After 4,4′-dinitro-2,2′-bis(*N*,*N*′-diethylcarbamoyl) biphenyl (4.42 g, 0.010 mol) was dissolved in 150 ml of ethanol at 60 °C, 1.00 g of Pt/C (5%) was added. After hydrazine monohydrate (5.00 ml) was added slowly, the solution was heated at reflux (80 °C) for 4 h. The precipitate, which formed during this time, was collected by filtration and washed with DMSO. The DMSO was distilled from the filtrate under reduced pressure to afford 2.50 g (65.4%) of a white powder: mp 324–326 °C; ^{1}H NMR (d-DMSO) δ 3.50 (m, 12H, C–H), 4.35 (m, 8H, C–H), 5.16 (s, 4H, N–H), 6.40 (d, 2H, Ar-H), 6.45 (s, 2H, Ar-H) and 6.80 ppm (d, 2H, Ar-H). Anal. calcd for $C_{22}H_{30}N_4O_2$: C, 69.08%; H, 7.91%; N, 14.65%. Found: C, 68.69%; H, 7.96%; N, 14.39%.

2.3. Model compound syntheses

*2.3.1. 4,4′-(p-Phenylene)bis(1,2,6,-triphenylpyridinium triflate) (**5a**)*

After 4,4′-(*p*-phenylene)bis(2,6-diphenylpyrylium triflate) (2.00 g, 0.00238 mol) was dissolved in 20.0 ml of dichloromethane, aniline (0.660 g, 0.00710 mol) was added. The solution, which became dark brown immediately, slowly turned red as it was stirred at room temperature for 2 h. The solution was poured into toluene. The precipitate that formed was collected by filtration to afford 2.02 g (85.9%) of light yellow powder: mp 338–340 °C; ^{1}H NMR (d-DMSO) δ 7.00–7.50 (m and br., 30H, Ar-H), 8.62 (s, 4H, Ar-H), and 8.75 ppm (s, 4H on pyridinium ring). Anal. calcd for $C_{54}H_{38}F_6N_2S_2O_6$: C, 65.58%; H, 3.87%; N, 2.83%. Found: C, 66.01%; H, 4.25%; N, 2.75%.

*2.3.2. 4,4′-(p-Phenylene)bis(1-(2,6-dimethylphenyl)-2,6-diphenylpyridinium triflate) (**5b**)*

This compound was synthesized by the same procedure used for preparing compound **5a**. 2,6-Dimethylaniline was used in place of aniline. 4,4′-(*p*-Phenylene)-bis(1-(2,6-dimethylphenyl)-2,6-diphenylpyridinium triflate) was obtained in 87.0% yield as a yellow powder: mp > 350 °C (decomposition); ^{1}H NMR (d-DMF) δ 3.50 (s, 12H, C–H), 7.0–7.8 (m, 26H, Ar-H), 8.90 (s, 4H, Ar-H), and 9.10 ppm (s, 4H on pyridinium ring). Anal. calcd for $C_{58}H_{46}F_6N_2S_2O_6$: C, 66.66%; H, 4.44%; N, 2.68%. Found: C, 66.28%; H, 4.66%; N, 2.51%.

*2.3.3. 4,4′-(p-Phenylene)bis(1-(3,4,5-trimethoxyphenyl)-2,6-diphenylpyridinium triflate) (**5c**)*

This compound was synthesized by the same method used for preparing compound **5a**. 3,4,5-Trimethoxyaniline was used in place of aniline. 4,4′-(*p*-Phenylene)-bis(1-(3,4,5-trimethoxyphenyl)-2,6-diphenylpyridinium triflate) was obtained in 79.5% yield as a yellow powder: mp > 350 °C (decomposition); ^{1}H NMR (d-DMF) δ 3.60 (s, 4H, C–H), 7.10 (s, 4H, Ar-H), 7.50 (m, 8H, Ar-H), 7.70 (m, 12H, Ar-H), 8.85 (s, 4H, Ar-H), and 8.98 ppm (s, 4H on pyridinium ring). Anal. calcd for $C_{60}H_{50}F_6N_2S_2O_{12}$: C, 61.64%; H, 4.31%; N, 2.40%. Found: C, 61.55%; H, 4.43%; N, 2.36%.

*2.3.4. 4,4′-(p-Phenylene)bis(1-(2-trifluoromethylphenyl)-2,6-diphenylpyridinium triflate) (**5d**)*

After 4,4′-(*p*-phenylene)bis(2,6-diphenylpyrylium triflate) (0.500 g, 0.000600 mol) was dissolved in 20.0 ml of DMSO, 2-trifluoromethylaniline (0.970 g, 0.00600 mol) was added. The solution was stirred at 100–120 °C for 12 h, during which time it turned from dark brown to light brown. The solution was poured into ether. The precipitate that formed was collected by filtration to afford 0.540 g (80.1%) of yellow powder: mp > 350 °C (decomposition); ^{1}H NMR (d-DMF) δ 7.6–7.9 (m, 26H, Ar-H), 8.5 (d, 2H, Ar-H), 8.92 (s, 4H, Ar-H), and 9.14 ppm (s, 4H on pyridinium ring). Anal. calcd for $C_{56}H_{36}F_{12}N_2S_2O_6$: C, 59.79%; H, 3.23%; N, 2.49%. Found: C, 59.88%; H, 3.49%; N, 2.38%.

2.4. Polymer syntheses

*2.4.1. Poly(pyridinium perchlorate) (**7b**)*

The procedure used for the polymerization was similar to the described method [21]. A solution of 4,4′-*p*-phenylene-bis(2,6-diphenylpyrylium) bisperchlorate (0.0400 mol) and benzidine (0.0400 mol) in 240 ml DMSO was heated in a 300-ml three-neck flask at 110–120 °C for 3 h under nitrogen. Then toluene (100 ml) was added so that water generated in the reaction could be removed as a toluene/water azeotrope. The azeotrope was gradually distilled from the reaction mixture at 120 °C using a Dean-stark trap over 10–12 h. The solution was then heated at 150–160 °C for 2–3 h to remove the toluene. The final solution was diluted with acetone and added to a large excess of water. The light yellow polymer that precipitated was collected by filtration and dried at 100 °C for 12 h.

*2.4.2. Poly(pyridinium tetrafluoroborate) (**7a**)*

The same procedure as used for **7b** was used. In this case, 4,4′-(*p*-phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) and benzidine were used as the monomers.

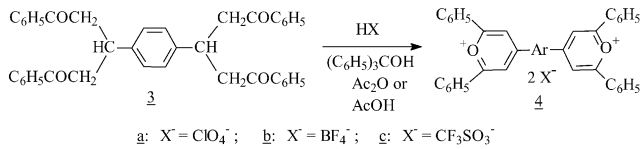
*2.4.3. Poly(pyridinium triflate)s (**7c–f, 14**)*

The procedure for the polymerization was analogous to that used for **7b**. In this case, however, the reaction time was much shorter (4–6 h). 4,4′-(*p*-Phenylene)bis(2,6-diphenylpyrylium triflate) and the following diamines were used in the polymerization: benzidine, 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl, 3,3′-dimethylbenzidine, 2,2′-dimethylbenzidine, and 4,4′-diamino-2,2′-bis(*N*,*N*′-diethylcarbamoyl)biphenyl.

3. Results and discussion

3.1. Synthesis of bis(pyrylium salt) monomers

Huang prepared pure 4,4′-(*p*-phenylene)bis(2,6-diphenylpyrylium triflate) by the acid-catalyzed ring closure of 3,3′-(*p*-phenylene)bis(1,5-diphenyl-1,5-pentanedione) (**4c**) in acetic anhydride [21]. Thus, an attempt was made to prepare 4,4′-(*p*-phenylene)bis(2,6-diphenylpyrylium perchlorate) (**4a**) and 4,4′-(*p*-phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) (**4b**) in this solvent (Scheme 1). However, pure products could not be obtained. Because aromatic bispyrylium salts are amorphous, they are more difficult to purify by common methods such as recrystallization. By comparing the ^{1}H NMR spectra of **4a**, **b** and **c**, it was possible to identify the major impurity in **4a** and **b** as the triphenylmethyl salt by-products generated during the syntheses. The salts display characteristic absorption peaks at 7.10–7.50 ppm.

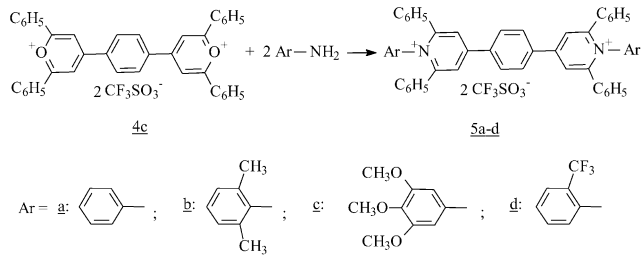


Scheme 1.

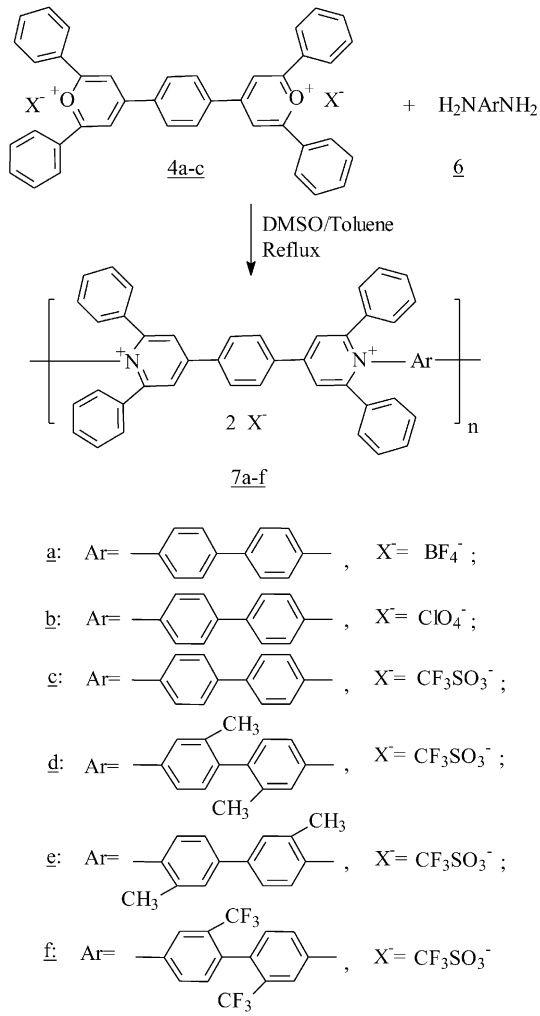
Several attempts to improve the reaction system led to the discovery that hot acetic acid is a good solvent for triphenylmethyl tetrafluoroborate and triphenylmethyl perchlorate. When the monomer syntheses were carried out in acetic acid at 90 °C, the by-products remained in solution and very pure products were obtained. The reaction time in acetic acid was also only 4 h, much shorter than required in acetic anhydride (12 h).

3.2. Synthesis of pyridinium salt model compounds

A series of model compounds (**5a–d**) was synthesized to aid in the study of the photobehavior of the poly(pyridinium salt)s (Scheme 2). Thus, 4,4′-(*p*-phenylene)bis(1,2,6,-triphenylpyridinium triflate) (**5a**) was prepared to simulate the repeat unit of a poly(pyridinium triflate) containing no substituents in the diamine component. 4,4′-(*p*-Phenylene)-bis[1-(2,6-dimethylphenyl)-2,6-diphenylpyridinium triflate] (**5b**) and 4,4′-(*p*-phenylene)bis[1-(3,4,5-trimethoxyphenyl)-2,6-diphenylpyridinium triflate] (**5c**) were prepared to determine the effects of electron-donating substituents on the photobehavior, while 4,4′-(*p*-phenylene)bis[1-(2-trifluoromethylphenyl)-2,6-diphenylpyridinium triflate] (**5d**) was prepared to determine the effects of electron-withdrawing substituents. Model compounds **5a–c** were synthesized in a mixture of methylene chloride and DMSO at room temperature. Model compound **5d** was prepared in DMSO at 100–120 °C for 12 h. The reaction had to be carried out at



Scheme 2.



Scheme 3.

elevated temperatures due to the reduced reactivity of the amine resulting from the electron-withdrawing trifluoromethyl group.

3.3. Synthesis of aromatic poly(pyridinium salt)s

Poly(pyridinium salt)s with different counter ions were synthesized in DMSO/toluene mixtures at elevated temperatures using the previously reported polymerization procedure (Scheme 3) [21]. The inherent viscosities and thermal properties of the poly(pyridinium salt)s are shown in Table 1. The viscosity of the poly(pyridinium tetrafluoroborate) was higher than that obtained previously ($\eta_{inh} = 4.5$ dl/g) [20], most likely due to the high purity of the bispyrylium tetrafluoroborate monomer. The data show that the thermal stability of poly(pyridinium salt)s depends on the counter ion. The more stable the counter ion, the more thermally stable the poly(pyridinium salt). This is in agreement with the results obtained by Huang et al. [21].

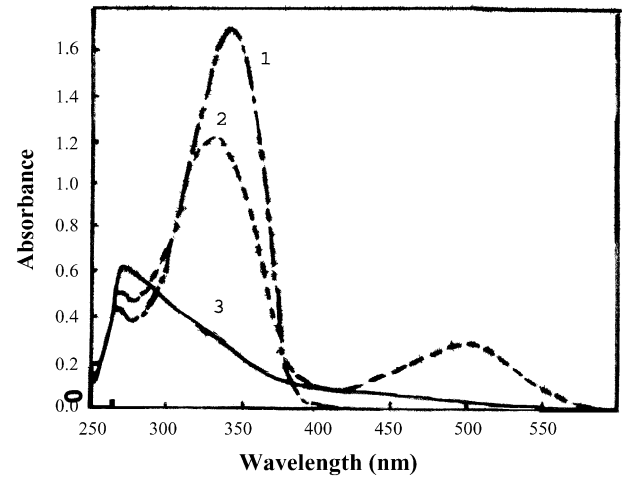
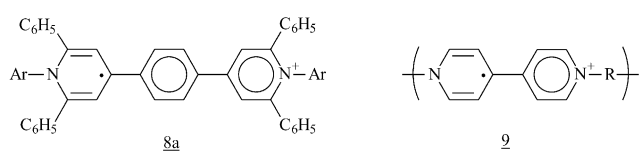


Fig. 1. UV–Vis spectra of model compound **5a** in DMF: curve 1 before irradiation; curve 2 after 1 min irradiation; curve 3 after 5 min irradiation.

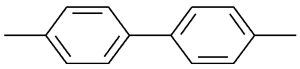
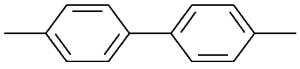
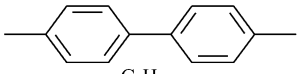
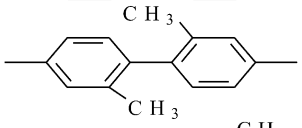
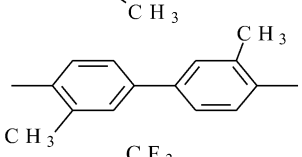
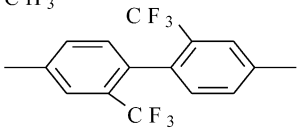
3.4. UV–Vis study of model compound solutions

The photochemical reactions of the model compounds **5a–d** were studied with UV–Vis spectroscopy. For example, the UV–Vis spectrum of a solution of model compound **5a** in DMF was recorded before and after UV irradiation (Fig. 1). The absorption peak at 342 nm characteristic of pyridinium salts [30] disappeared gradually and a new absorption peak near 500 nm first appeared and then disappeared after it reached a maximum. It was speculated that the absorption at 500 nm was due to the formation of radical cations (**8a**). The radical cations formed by the irradiation of viologen oligomers (**9**) display characteristic



absorption maxima at 525–540 nm [14]. Although films containing viologens display absorption maxima near 600 nm [15], the absorption maxima of polymers containing pendent viologen units in aqueous solutions are near 530 nm [12]. The hypsochromic shifts of the absorption peaks in solution have been attributed to the aggregation of the viologen cation radicals. In the model compounds, the aromatic ring located between the pyridine rings would be expected to decrease the interaction between the positively charged nitrogen and the free radical relative to that in viologens. After irradiation for 5 min, only one absorption at 270 nm, which is characteristic of aromatic rings, remained. Simultaneously, the solution turned from yellow to deep red and then to light yellow. All of the changes were irreversible. The photoreduction of some low molecular weight viologens in amide solvents are also irreversible and produce secondary reaction products [19]. No evidence was found for photocyclizations reported by Katritzky to take place

Table 1
Properties of poly(pyridinium salt)s

	–Ar–	X^-	η_{inh} (dl/g)[a]	T_d (°C)[b] (Air)	T_d (°C)[b] (N_2)
7a		BF_4^-	7.5	325	328
7b		ClO_4^-	6.4	290	289
7c		$CF_3SO_3^-$	8.4	463	464
7d			7.2	450	453
7e			7.0	420	421
7f			6.3	425	424

[a] Inherent viscosity was measured at a concentration of 0.2 g/dl at 30.0 ± 0.1 °C in DMSO.
[b] Temperature at which a 5 wt% loss occurred when the polymers were subjected to TGA with a heating rate of 10 °C/min.

when 1,2-diarylpyridinium cations are irradiated with short wavelength UV light [31,32].

The dependence of the absorbance of model compound **5a** at 342 nm on the UV irradiation time in different solvents is shown in Fig. 2. The photoreaction occurred only in amide solvents like DMF or DMAc. No photoreaction occurred in DMSO. The UV–Vis spectra of model compounds **5a**–**d** were also measured in NMP before and after irradiation. The changes in the absorbance at 342 and 500 nm were recorded as a function of UV irradiation time (Figs. 3 and 4). The rate of the photoreaction was influenced by the substituents on the phenyl ring attached to the positively charged nitrogen. Electron-withdrawing trifluoromethyl substituents accelerated the rate, while electron-donating methoxy substituents slowed the rate. This is consistent with the formation of radical cations from the parent dications. Kamogawa obtained similar results when viologen compounds containing electron-donating and electron-withdrawing groups were mixed with poly(vinylpyrrolidinone), which has pendent amide groups [18].

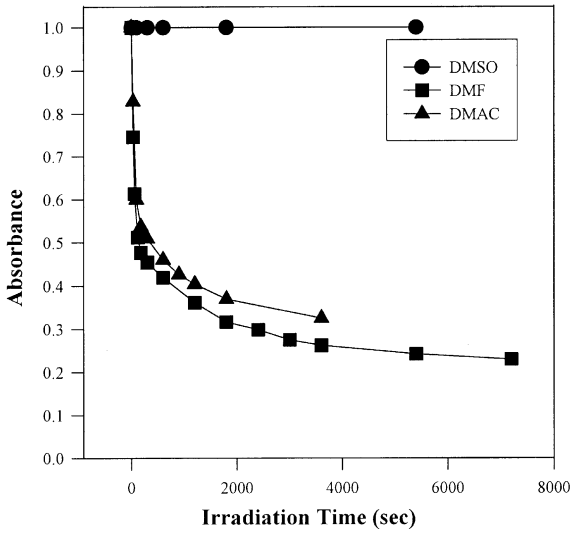


Fig. 2. Dependence of absorbance of model compound **5a** at 342 nm on exposure time to UV–Vis irradiation in different solvents.

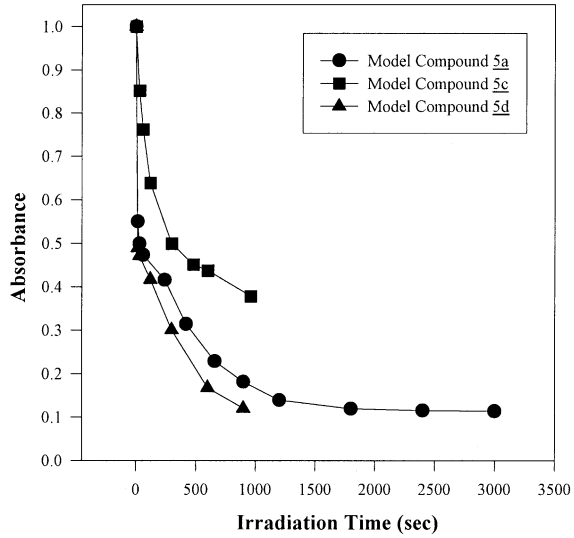


Fig. 3. Dependence of absorbances of model compounds **5a**, **c**, and **d** at 342 nm on exposure time to UV–Vis irradiation in NMP.

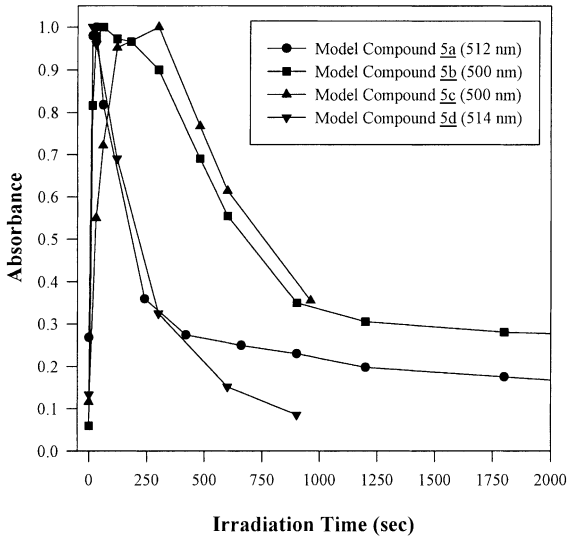
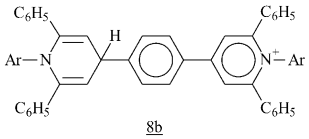


Fig. 4. Dependence of absorbances of model compounds **5a–d** near 500 nm on exposure time to UV–Vis irradiation in NMP.

3.5. ^{1}H NMR study of the photoreduction of model compounds

A preliminary ^{1}H NMR study of the photoreduction of the model compounds has also been carried out [33]. The compounds were dissolved in deuterated DMF and irradiated over extended periods of time. The ^{1}H NMR spectra of the highly colored species generated initially were consistent with that of radical cation structures (**8a**). Upon further irradiation, the spectra changed to be consistent with mono pyridinium salt structures (**8b**). This process was



8b

probably facilitated by the amide solvent, which is known to act as a hydrogen radical donor under UV irradiation [34]. After long-term irradiation, the absorptions that were attributed to the protons on the pyridinium ring disappeared, and the spectra became quite complex. The rate at which these spectral changes took place were dependent on the amine residue substituents. Electron-withdrawing groups accelerated the changes, while electron-donating groups slowed the process. A more comprehensive NMR study is currently in progress.

3.6. UV–Vis study of poly(pyridinium salt) solutions

A series of solutions of the poly(pyridinium salt)s in different solvents was prepared and irradiated with UV light. The color of the solutions of **7c** in amide solvents such as DMF, NMP and DMAc changed during the irradiation. No color change occurred in non-amide solvents such as DMSO and formic acid. The initial UV–Vis spectra of

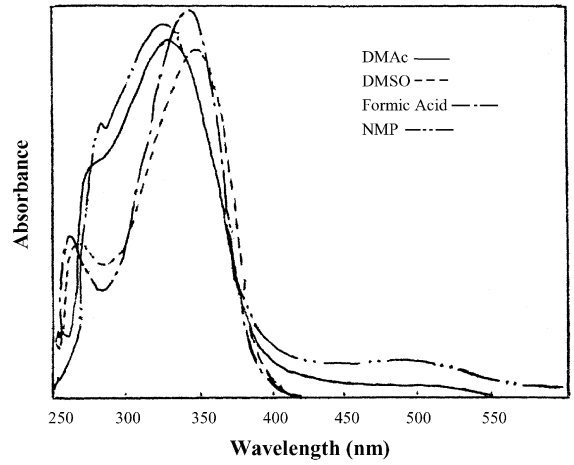


Fig. 5. UV–Vis spectra of poly(pyridinium triflate) **7c** in different solvents.

poly(pyridinium triflate) **7c** in different solvents are shown in Fig. 5. The UV–Vis spectra of the poly(pyridinium triflate) DMF solutions after different periods of UV irradiation are shown in Fig. 6. The photobehavior was nearly identical to that displayed by model compound **5a** in DMF. The main absorption peak at 348 nm disappeared gradually as the time of exposure to UV–Vis irradiation increased. A new absorption at 500 nm appeared immediately and then disappeared after it reached a maximum. After irradiation for 5 min, only one absorption at 270 nm, characteristic of aromatic rings, remained. At the same time,

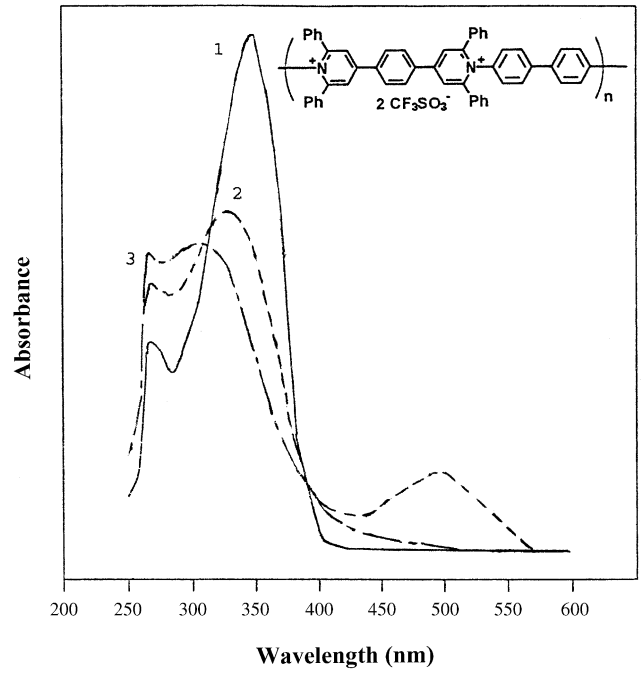


Fig. 6. UV–Vis spectra of poly(pyridinium triflate) **7c** in DMF: curve 1 before irradiation; curve 2 after 1 min irradiation; curve 3 after 5 min irradiation.

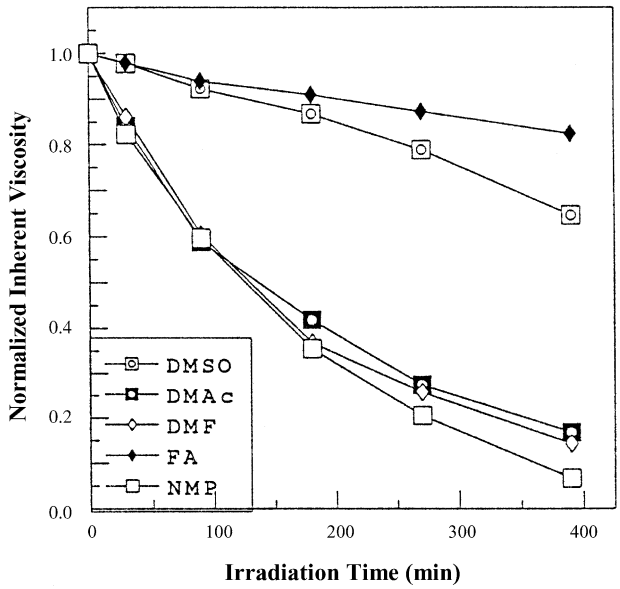


Fig. 7. Normalized inherent viscosities of poly(pyridinium triflate) **7c** as a function of exposure to UV–Vis irradiation in different solvents in air.

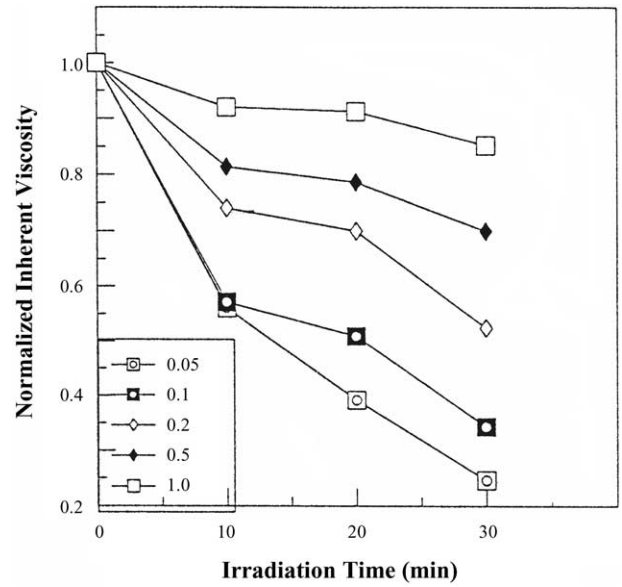


Fig. 9. Normalized inherent viscosities of poly(pyridinium triflate) **7c** as a function of exposure to UV–Vis irradiation and concentration (wt%) in DMF.

the color of the solution turned from yellow to red and then light yellow. All the changes were irreversible.

3.7. Viscosity study of poly(pyridinium salt)s under UV irradiation

The inherent viscosities of the poly(pyridinium salt)s were examined in different solvents under UV–Vis irradiation. The effects of counter ions, concentration, solvents and backbone substituents on the polymer inherent viscosity were investigated. The results are shown in Figs. 7–11. The inherent viscosity of the poly(pyridinium triflate) **7c** decreased dramatically with increasing exposure to UV–Vis irradiation in amide solvents such as DMF, DMAc and NMP (Fig. 7). The viscosity decrease also occurred when the solutions were irradiated under nitrogen (Fig. 8). The viscosity of the poly(pyridinium triflate) in non-amide solvents decreased very slowly under UV–Vis irradiation.

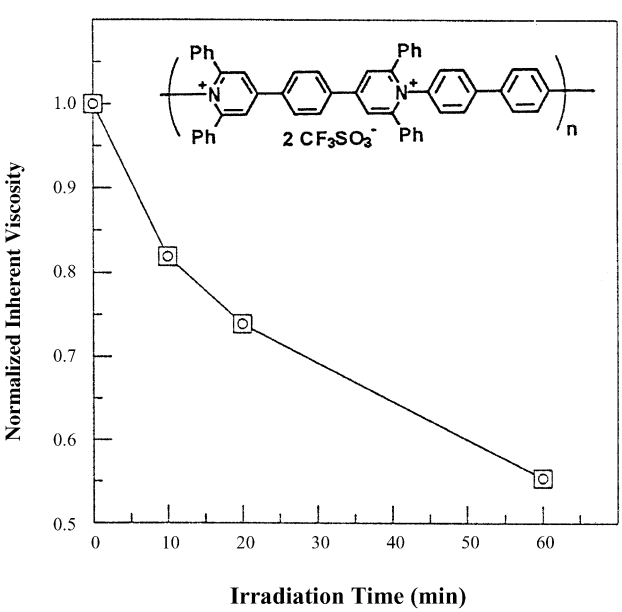


Fig. 8. Normalized inherent viscosities of poly(pyridinium triflate) **7c** as a function of exposure to UV–Vis irradiation in DMF in nitrogen.

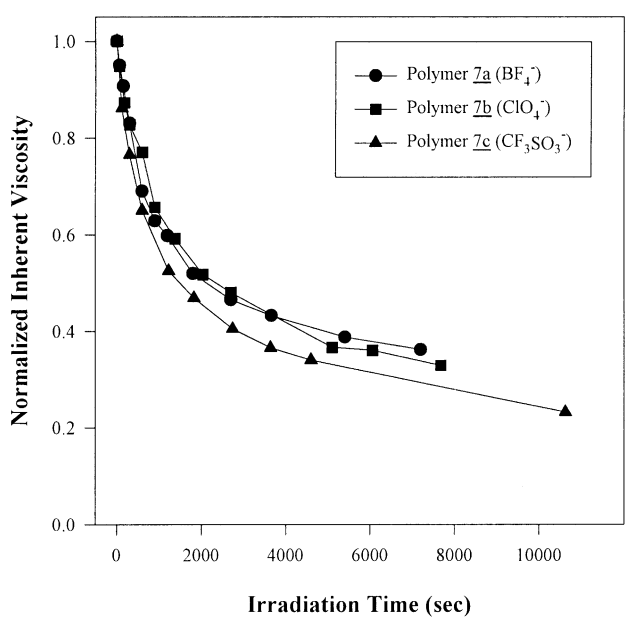


Fig. 10. Normalized inherent viscosities of poly(pyridinium salt)s **7a–c** as a function of exposure to UV–Vis irradiation.

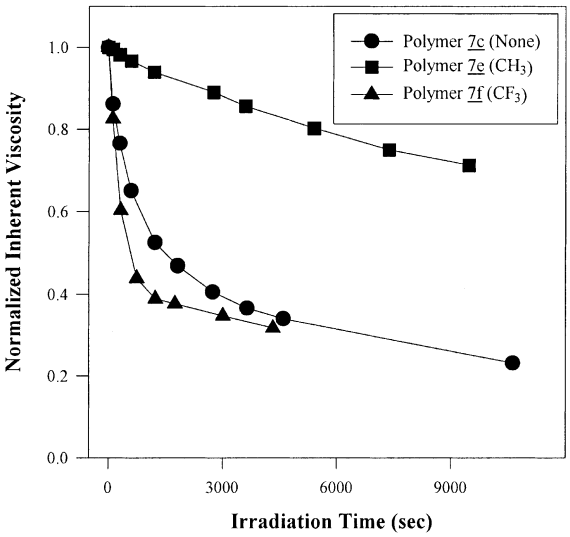
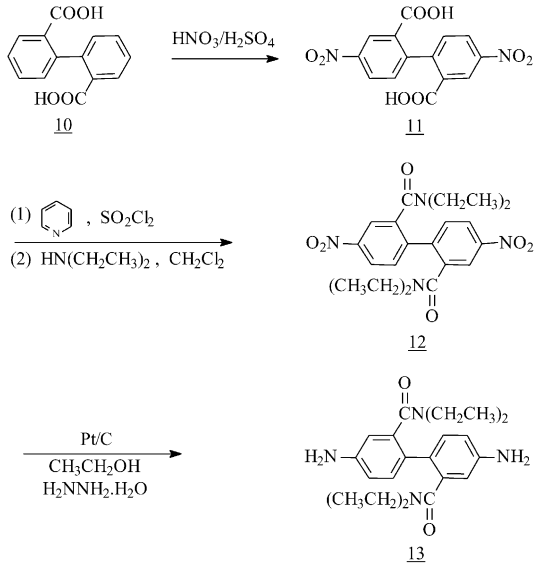


Fig. 11. Normalized inherent viscosities of poly(pyridinium salt)s **7c**, **e**, and **f** as a function of exposure to UV–Vis irradiation.



Scheme 4.

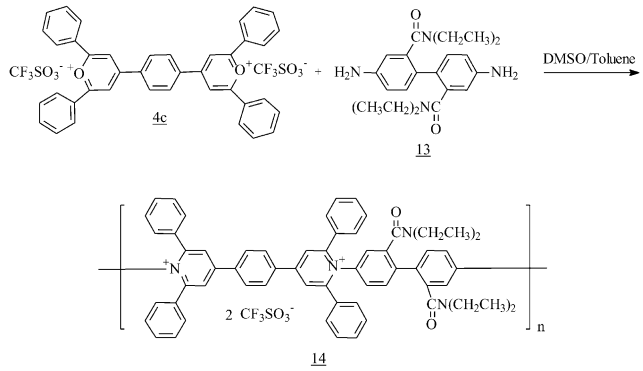
This is consistent with the results discussed in the previous sections. The higher the concentration of the poly(pyridinium triflate) in DMF, the more stable the polymer was to UV irradiation (Fig. 9). This suggests that the active state generated was subject to quenching. There was no significant effect of the counter ions of the poly(pyridinium salt)s on the stability of the polymers in amide solvents (Fig. 10). This suggests that the ions did not play a major role in the decomposition process. The substituents on the biphenyl units in the backbones of the poly(pyridinium salt)s, however, had a significant effect on the stability of the polymers in DMF (Fig. 11). Methyl groups (electron-donating groups) dramatically increased the stability of the polymers, while trifluoromethyl groups (electron-withdrawing groups) resulted in a faster decrease in viscosity.

The rapid decreases in inherent viscosity are likely related to the loss of the positive charges located along the polyelectrolyte backbones. The almost total loss of viscosity in some cases, however, suggest that backbone cleavage must also have taken place. It is speculated that this could have occurred through hydrolysis of the reduced intermediates by fortuitous water in the amide solvents. Photoreductions are currently being carried out under anhydrous conditions to test this hypothesis and to further aid in the determination of the photodecomposition mechanisms.

3.8. Synthesis and photobehavior of a poly(pyridinium triflate) containing pendent amide groups

In order to verify that the photoreaction of pyridinium salts in amide solvents involves the amide groups, a model poly(pyridinium triflate) (**14**) containing pendant amide groups was prepared (Scheme 5). Monomer **13** was prepared first by the reaction sequence shown in Scheme 4. Thus, diphenic acid (**10**) was nitrated with a mixture of nitric and sulfuric acid to yield the dinitro-substituted intermediate **11**. Treatment of **11** with thionyl chloride followed by the addition of diethylamine gave the diamine **12**, which was reduced with hydrazine monohydrate to yield the diamine monomer **13**. The monomer was then polymerized with **4c** in a DMSO/toluene mixture using the previously developed procedure (Scheme 5).

As shown in this work, poly(pyridinium salt)s undergo only a slight decrease in viscosity when subjected to UV irradiation in non-amide solvents such as DMSO. But when an attempt was made to measure the inherent viscosity of polymer **14** in DMSO, the data were inconsistent, and the viscosity appeared to be decreasing during the measurement. This is the same type of behavior observed when attempts were made to measure the inherent viscosities of poly(pyridinium salt)s in amide solvents. Solutions of polymer **14** in DMSO were then irradiated for various periods of time (Fig. 12). The fact that the polymer viscosity decreased affords additional evidence that the photoreaction



Scheme 5.

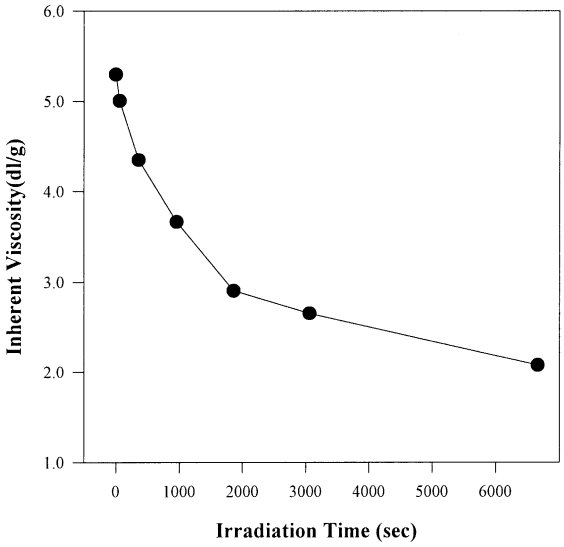


Fig. 12. Inherent viscosities of poly(pyridinium triflate) **14** as a function of exposure to UV–Vis irradiation in DMSO.

of poly(pyridinium salt)s was facilitated by amide groups. Interestingly, films of polymer **14** changed from yellow to light brown upon exposure to UV light. Unlike in solution, the photoreduction in the solid state was reversible. When the UV light was turned off, and the films were stored in air they once again became yellow. However, the films remained brown when they were stored under reduced pressure or in nitrogen. This photochromic behavior likely involves the interaction of the amide groups with the reduction sites to generate radical cations that are subsequently oxidized in air. The process is currently under investigation.

4. Conclusions

Poly(pyridinium salt)s readily undergo photodecomposition in amide solvents. Although the mechanism of the complete decomposition process is not known, there is considerable evidence that the process proceeds through the initial formation of radical cations. The rate of radical formation is increased by the presence of electron-withdrawing groups and decreased by the presence of electron-donating groups. It is also clear that amide groups facilitate the formation of the radical cations. In fact, it is speculated that amide groups may serve as reducing agents providing the electrons in the electron transfer process. Evidence for this comes from the fact that the poly(pyridinium salt) counter anion, which has been reported to serve as the electron source in viologen photoreductions [17], does not appear to affect the process. A poly(pyridinium triflate) containing pendent amide groups also undergoes photoreduction in DMSO, in marked contrast to the photostability displayed by the unsubstituted parent polymer in this solvent.

Acknowledgements

The support of this research by the Division of Materials Research of the National Science Foundation (DMR 89-20147) through the Science and Technology Center on Advanced Liquid Crystalline Optical Materials (ALCOM) at Kent State University, Case Western Reserve University and The University of Akron is gratefully acknowledged.

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