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Articles

Synthesis and Characterization of Poly(pyridinium salt)s with Organic Counterions Exhibiting Both Thermotropic Liquid-Crystalline and Light-Emitting Properties

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ABSTRACT: Two poly(pyridinium salt)s with bulky organic counterions (tosylate and triflimide) were synthesized by either the ring-transmutation polymerization reaction of 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium tosylate) with 1,12-diaminododecane on heating in dimethyl sulfoxide (DMSO) at 145−150 °C for 24 h or the metathesis reaction of the corresponding tosylate polymer with lithium triflimide in a common organic solvent such as acetonitrile. Their polyelectrolyte behavior in DMSO was determined by solution viscosity measurements, and their chemical structures were determined by Fourier transform infrared and Fourier transform NMR spectroscopy. They were characterized for their thermotropic liquid-crystalline properties with a number of experimental techniques. Poly(pyridinium salt) with tosylate as a counterion had a crystal-to-smectic phase transition at 116 °C that persisted up to its decomposition temperature. The corresponding polymer with triflimide as a counterion had not only lower crystal-to-smectic phase transition at 80 °C but also a smectic-to-isotropic transition at about 180 °C. Both of these transitions were well below its decomposition temperature. It had better thermal stability than that of the corresponding tosylate polymer. Their fluorescence property in solutions of tetrahydrofuran and methanol as well as in the solid state was also included in this study.

Introduction

In recent years, nitrogen-containing polymers have received unabated attention in the design and synthesis of electroluminescent polymers. They generally consist of π-electron-deficient heterocycles containing imine nitrogen in the aromatic moieties.[1−11] Unlike other π-conjugated polymers,[12−15] they contain nitrogen heteroatom either in the main chains or in the side chains that provide facile quaternization reaction and protonation of the nitrogen sites. Thus, their emission spectra can be tuned at will by adding a charged species to the nitrogen site via by manipulating their electronic structures.[1−11] Besides their electroluminescent properties,[1−11] conducting[16] and liquid-crystalline (LC)[17−19] properties of suitably designed polymer structures make them attractive materials in many technological applications. However, the two other main-chain poly(pyridinium salt)s are of considerable interest. One typically consists of 4,4′-bipyridinium ions along the backbone of the polymer chains that are known as viologen polymers. They exhibit a number of interesting properties including electrical conductivity,[20] electrochromism,[21] photochromism,[22] thermochromism,[23] and LC properties.[24−28] The other consists of 4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium) ions along the backbone of the polymer chains. They, like viologen polymers, also exhibit a number of unique properties that include redox behavior, electrochromism, conductivity when doped with 7,7,8,8-tetracyanoquinodimethane, and photochromism.[29] Harris et al. reported the synthesis of this class of polymers containing $^{-}BF_4$, an inorganic counterion, by the ring-transmutation polymerization reaction of 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) with various aromatic diamines and the characterization of their physical properties. Although their glass transition, T_g, values cannot be determined by the DSC measurements, they exhibit distinct melting endotherms with a minimum above 380 °C. The TGA measurements indicate that they start to decompose at about 360 °C prior to their melting transition, T_m, values. Even the two poly(pyridinium salt)s containing flexible oxyethylene linkages in the aromatic diamines moieties gradually decompose above 250 °C as determined by DSC measurements. Their T_g values also cannot be determined by this technique. However, the dynamic mechanical thermal analysis (DMTA) clearly shows a transition near 260 °C, which is related to the decomposition as the tan δ value goes off the scale. These two polymers soften into a black tar and emit smoke at about 260 °C. Their wide-angle X-ray diffraction (WAXD) patterns reveal

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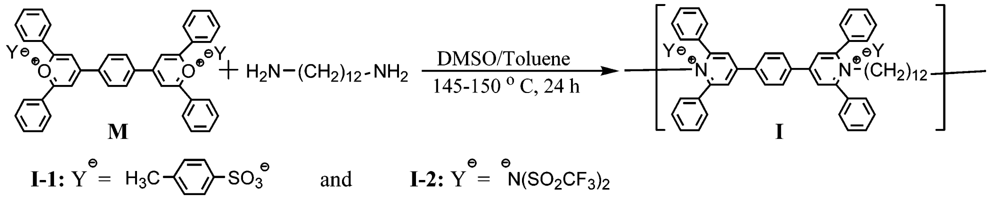
Scheme 1



that they are highly crystalline. Despite the presence of ionic groups in these polymers, they are insoluble in water but soluble to a limited extent in polar aprotic solvents and can be solution cast into tough, flexible films. Additionally, the extent of their solubility in these solvents is insufficient to form lyotropic solutions.[29] Recently, Huang et al. reported the results of another series of poly(pyridinium salt)s with triflate as an organic counterion. These polymers are significantly more thermally and thermooxidatively stable than analogous poly(pyridinium salt)s with $^{-}BF_4$ counterion. Like the poly(pyridinium salt)s with $^{-}BF_4$ as a counterion, the T_g values of these polymers also cannot be detected by DSC measurements below 400 °C. Although WAXD patterns indicate their low degree of crystallinity, no melting transitions could be detected below 400 °C. Evidently they also decompose prior to melting transition. They are also soluble in polar organic solvents including dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and dimethylacetamide (DMAc), from which fingernail creasable films are easily cast.[30] Bhowmik et al.[31] reported another series of poly(pyridinium salt)s with tosylate as a counterion that exhibit a lyotropic LC phase in DMSO and methanol as well as fluorescent properties in these solvents. Other poly(pyridinium salt)s have also received considerable attention because of their photoluminescence properties.[32−35]

In this article, we describe the synthesis of two new ionic polymers—poly(pyridinium salt)s—containing bulky organic counterions such as tosylate and triflimide ions and the characterization of their thermotropic LC properties. The general structure and designations of these ionic polymers, **I**, which were prepared and characterized in this study, are shown in Scheme 1. They are the first examples of poly(pyridinium salt)s with both tosylate and triflimide as counterions that exhibit thermotropic LC properties. They also exhibit photoluminescence both in solution and in the solid state.

Experimental Section

Monomer Synthesis. The 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium)ditosylate, **M**, was synthesized by the modification of a procedure by which the corresponding bis(tetrafluoroborate) salt was prepared.[29] In this procedure, terephthalaldehyde was condensed with more than the 4 mol of acetophenone to afford the desired tetraketone, which was subsequently cyclodehydrated to **M** by treatment with triphenylmethyl tosylate. The hydride acceptor was generated in situ from triphenylmethanol and tosic acid. It was recrystallized from acetic acid (yield 75%). It showed several endothermic transitions at 161 (T_m), 195, and 304 °C (T_i) as determined by DSC at a heating rate of 10 °C/min.[33] Its purity was also checked by ^{1}H NMR spectroscopy and elemental analysis. δ_H (d_6-DMSO, 400 MHz, ppm): 9.35 (4H, s, aromatic meta O$^+$), 9.21 (4H, s, 1,4-phenylene), 7.58−8.93 (20H, m, phenyl), 7.46−7.47 (4H, d, J = 6.7 Hz, tosylate), 7.09−7.10 (4H, d, J = 7.7 Hz, tosylate), and 2.27 (6H, s, CH$_3$). Anal. Calcd for $C_{54}H_{42}O_8S_2$: C, 73.45; H, 4.79; S, 7.26. Found: C, 71.25; H, 4.71; S, 7.41. This compound is somewhat hygroscopic and highly charged and, therefore, poses difficulties in burning completely. In this case, the absolute values are not correct, and it is necessary to introduce the ratios C/O = 4.28, C/S = 9.61, and S/O = 0.45, which are quite agreement with the theoretical values (C/O = 5.06, C/S = 10.12, and S/O = 0.50).[36]

The 1,12-diaminododecane was received from Sigma-Aldrich Chemical Co. and further purified by sublimation under vacuum. Anal. Calcd for $C_{12}H_{28}N_2$: C, 71.93; H, 14.09; N, 13.98. Found: C, 72.15; H, 14.04; N, 14.24.

Synthesis of Polymer I-1. The bis(pyrylium) salt **M** was polymerized with 1,12-diaminododecane by ring-transmutation polymerization reaction to yield polymer **I-1** that was carried out on heating in DMSO as shown in Scheme 1. The water generated during the polymerization reaction was distilled from the reaction medium as a toluene/water azeotrope. The polymer was essentially isolated in quantitative yield by precipitation with the addition of distilled water. IR (neat): ν (cm^{-1}) 3058, 2925, 2853, 1619, 1596, 1558, 1495, 1448, 1392, 1199, 1120, 1033, 1012, 777, 701, 679, 568. δ_H (d_6-DMSO, 400 MHz, ppm): 8.60 (4H, d, aromatic meta to N$^+$), 7.50−8.50 (24H, m, aromatic), 7.47−7.49 (4H, d, J = 7.9 Hz, tosylate), 7.07−7.09 (4H, d, J = 7.8 Hz, tosylate), 3.36 (4H, m, N$^+$-CH$_2$), 2.26 (6H, s, CH$_3$), 0.68−1.45 (20H, m, CH$_2$). δ_C (d_6-DMSO, 100 MHz, ppm): 156.64, 156.54, 155.89, 153.21, 152.37, 148.79, 147.96, 145.76, 141.12, 138.70, 138.56, 137.38, 136.17, 133.69, 132.94, 132.82, 130.77, 129.54, 129.14, 128.92, 128.66, 128.37, 127.89, 126.94, 126.39, 126.02, 125.38, 116.58, 54.15, 28.41, 28.09, 27.23, 25.18, 20.66. Anal. Calcd for $C_{66}H_{66}N_2O_6S_2$ (**I-1**): C, 75.69; H, 6.35; N, 2.67; S, 6.12. Found: C, 76.02; H, 6.75; N, 2.94; S, 5.77.

Synthesis of Polymer I-2. It was prepared by the metathesis reaction of polymer **I-1** with lithium triflimide in a common organic solvent such as acetonitrile. The procedure that was employed is described as follows. One gram (0.95 mmol) of polymer **I-1** was dissolved in 25 mL of acetonitrile on gentle warming. To the acetonitrile solution of this polymer, 25 mL of acetonitrile solution of lithium triflimide (1.2 g, 4.2 mmol) was added dropwise on stirring. The resulting solution was kept at 50 °C overnight with stirring. After removing acetonitrile by a rotary evaporator completely, distilled water was added to the solid products to dissolve both lithium tosylate and excess lithium triflimide, affording the desired polymer **I-2**. It was collected by filtration, washed several times with a large quantity of distilled water, and dried in a vacuum at 50 °C for 48 h and weighed to give 1.1 g (0.87 mmol) of polymer **I-2** (yield 92%). Anal. Calcd for $C_{56}H_{52}N_4O_8F_{12}S_4$ (**I-2**): C, 53.16; H, 4.14; N, 4.43; S, 10.14. Found: C, 56.68; H, 4.96; N, 4.35; S, 9.03.

Polymer Characterization. The FTIR spectra of polymers were recorded with a Nicolet FTIR analyzer with their neat films on KBr pellets. Their ^{1}H and ^{13}C NMR spectra were recorded with a Brüker AM 400 spectrometer with three RF channels operating at 400 and 100 MHz, respectively, in d_6-DMSO using TMS as an internal standard. Inherent viscosities (IVs) of the polymers were measured in DMSO at various concentrations with a Cannon Ubbelohde viscometer at 35 °C. Phase transition temperatures were measured with a TA 2100 differential scanning calorimeter under a nitrogen flow at heating and cooling rates of 10 °C/min. The temperature axis of the DSC thermogram was calibrated before use with the reference standard of high-purity indium and tin. Polymers usually weighing 8−10 mg were used for this analysis. The thermogravimetric analysis (TGA) was performed with a TA

2100 instrument at a heating rate of 10 °C/min in nitrogen. The thermomchanical analysis (TMA) was conducted by using Netzsch TMA 202 instrument. These experiments were run at 10 °C/min from 25 to 250 °C under nitrogen (50 mL/min) with a constant force of 10 cN applied to the sample. The polarizing light microscope (PLM) studies were performed with a polarizing light microscope (Nikon, model Labophot 2) equipped with crossed polarizers and a hot stage. X-ray studies of polymer **I-2** were carried out at the Advanced Photon Source of Argonne National Laboratory using the Midwestern Universities Collaborative Team's beamline on Sector 6. It was sealed in 1 mm diameter Lindeman capillary and aligned in the presence of a magnetic field of ~2.5 kG on cooling to LC phase from the isotropic phase. Sample temperature was controllable with a precision of ±0.1 °C using homemade oven and temperature controller. A wavelength of 0.7653 Å was used. The diffraction patterns were collected using a high-resolution MAR3450 area detector placed at a distance of 586.62 mm from the sample. Absorption spectra of polymers in spectrograde tetrahydrofuran and CH_3OH were recorded with a Varian Cary 3 Bio UV–vis spectrophotometer at ambient temperature. Their photoluminescence (PL) spectra both in solutions and in solvent cast thin films were recorded with a Perkin-Elmer LS 55 luminescence spectrometer with a xenon lamp light source.

Results and Discussion

Chemical Structures. The ^{1}H and ^{13}C NMR spectra of polymer **I-1** in d_6-DMSO are consistent with its proposed structure. Furthermore, its ^{13}C NMR spectrum contains only aromatic carbon signals between 96 and 136 ppm. The carbonyl resonance at ca. 187 ppm, which is attributable to a vinylogous amide,[37] was not detected, suggesting that the ring-transmutation polymerization reaction proceeded to completion. The proton signals of vinylogous amide and amino end groups were also not detected in its ^{1}H NMR spectrum. The FTIR spectrum of polymer **I-2** at room temperature on KBr pellets that contains the following characteristic absorption bands: 3063 (=C–H aromatic stretching), 2928, 2856 (C–H aliphatic stretching), 1620 (C=C aromatic ring stretching), 1495 (C–H aliphatic bending), 1351 (C–F stretching), 1193 (H_2C-N^+), 1134 (S=O asymmetric stretching), 1058 (S=O symmetric stretching), and 778 cm^{-1} (=C–H out-of-plane bending). The ^{1}H and ^{13}C NMR spectra of polymer **I-2** in d_6-DMSO are consistent with its proposed structure. The absence of tosylate proton signals suggested that exchange of tosylate ion with triflimide was effective in the metathesis reaction under the experimental conditions used.

Solution Properties. Because of the presence of 4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium) ions along the backbone of the polymer chain, each of these polymers, **I-1** and **I-2,** showed a polyelectrolyte behavior in DMSO. However, polymer **I-1** containing tosylate as a counterion exhibited a drastic increase in inherent viscosity with dilution, and an intense maximum appeared in a very dilute concentration (3.8×10^{-4} mol/L) regime. Such a strong peak made it difficult to extrapolate the inherent viscosity to $C = 0$ and determine intrinsic viscosity, $[\eta]$.[38] In contrast, polymer **I-2** containing triflimide as a counterion exhibited a gradual increase in inherent viscosity with the decrease in polymer concentration and also obeyed the empirical Fuoss equation,[39] which is usually applied to random coiled polyelectrolytes: $\eta_{inh} = A/(1 + BC^{0.5}) \Rightarrow (\eta_{inh})^{-1} = 1/A + B/AC^{0.5}$, where A and B are constants; η_{inh} and C are usual notations. Its $[\eta]$ value obtained from the intercept of Fuoss plot was 0.27 dL/g in DMSO at 35 °C. Although its $[\eta]$ value was rather low, the absence of end groups in its ^{1}H NMR spectrum was indicative of reasonably high molecular weight. Furthermore, it had fingernail-creasable film-forming properties from a number of common organic solvents that included tetrahydrofuran, chloroform, methanol, acetonitrile, and DMSO. These statements are equally applicable to polymer **I-1**.

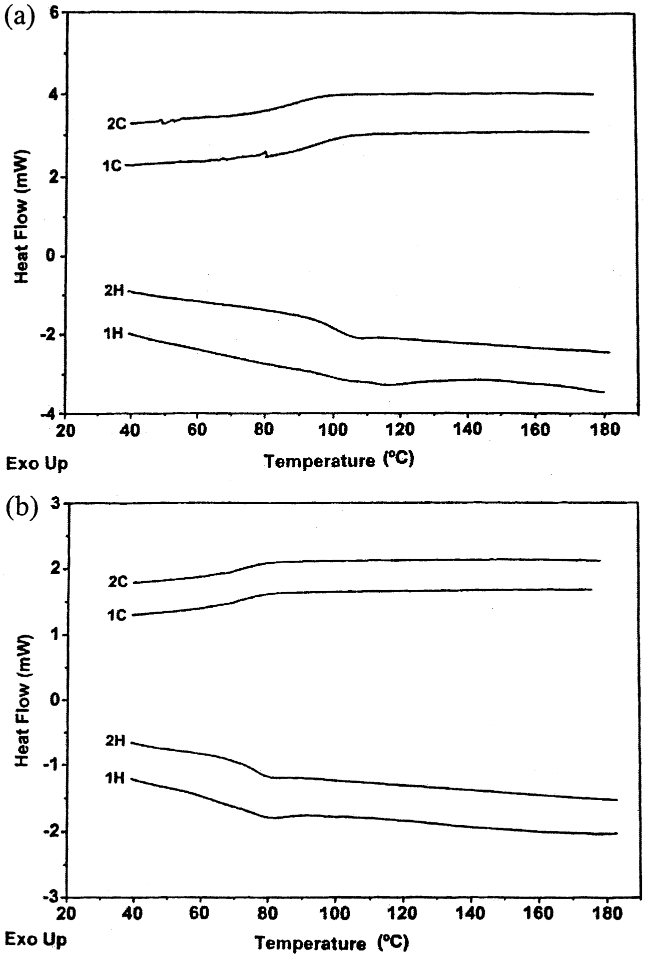


Figure 1. DSC thermograms of polymers **I-1** and **I-2** obtained at both heating and cooling rates of 10 °C/min: (a) and (b), respectively.

Thermotropic Liquid-Crystalline Properties. Poly(pyridinium salt)s with either $^-BF_4$ or triflate as a counterion do not exhibit thermotropic LC properties because of their thermal decomposition prior to melting transitions.[29,30] In contrast, polymer **I-1** containing tosylate as a counterion showed a complex crystal-to-LC transition, T_m, at 116 °C (heating rate 10 °C/min), above which it formed a viscous melt. On further heating to higher temperature, it exhibited an additional LC transition at 230 °C that extended up to its thermal decomposition at 254 °C. This decomposition temperature was obtained at a heating rate of 10 °C/min in nitrogen by TGA measurement at which 5% weight loss of polymer **I-1** occurred. This transition was also verified by the visual observation of the development of new LC texture at the expense of the originally complex texture with the PLM studies. The T_m of this polymer was reproducible and reversible when it was run up to 200 °C that was well below the decomposition temperature, since this transition appeared at each of the heating cycles of DSC thermograms (Figure 1a). The T_m was also verified with TMA measurement (Figure 2a). Figure 3a shows the photomicrograph of polymer

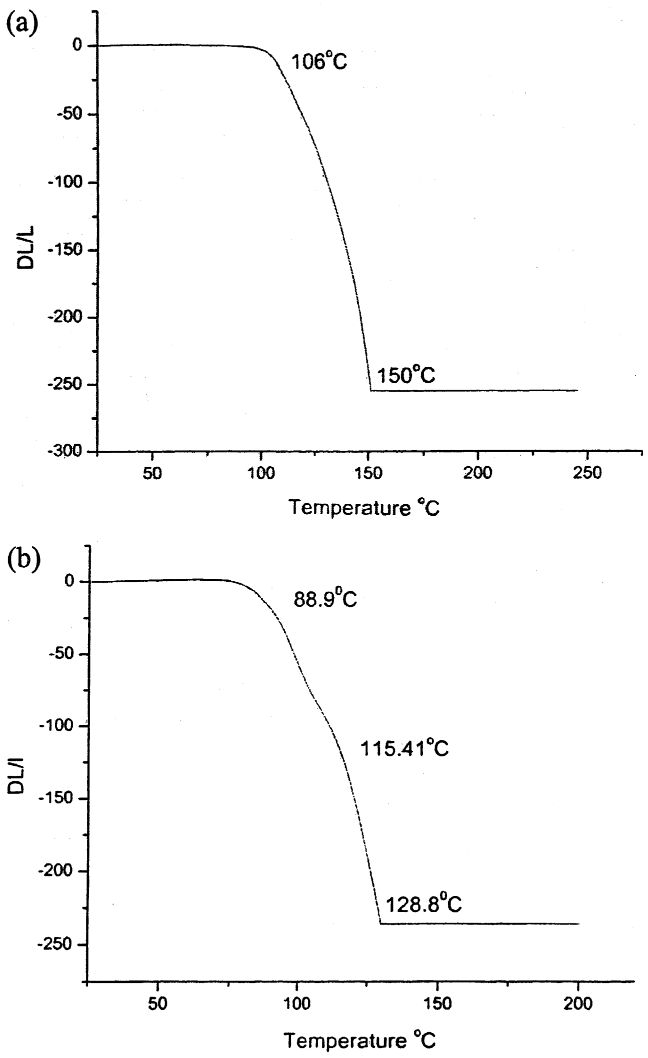


Figure 2. TMA plots of polymers **I-1** and **I-2** with a heating rate of 10 °C/min and a load force of 10 cN: (a) and (b), respectively.

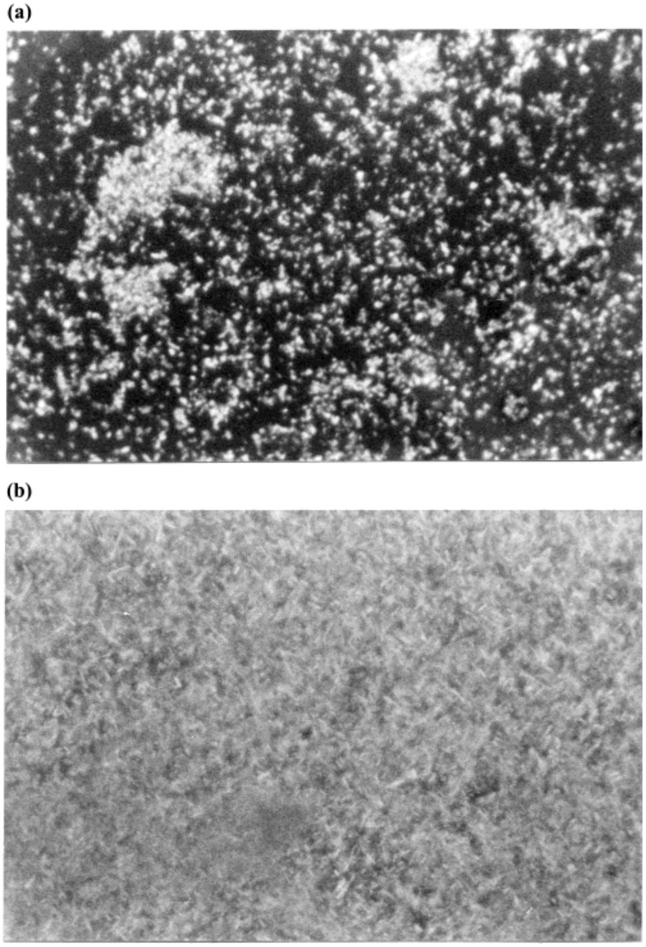


Figure 3. Photomicrographs of polymer **I-1** taken at 220 °C and of polymer **I-2** taken at 110 °C under crossed polarizers exhibiting (a) and (b) smectic LC phases, respectively (magnification 400×).

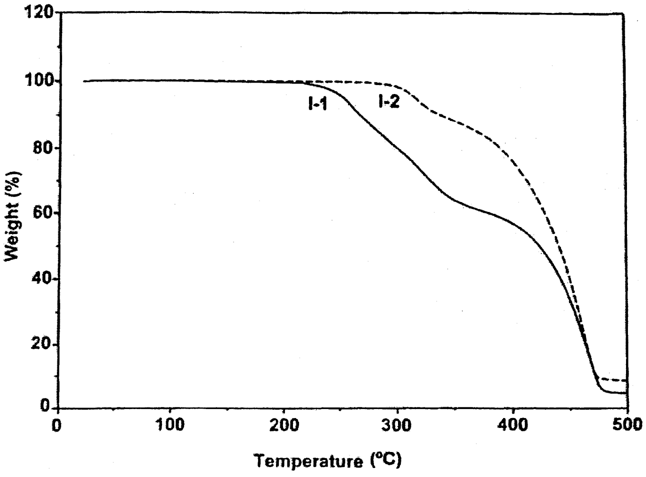


Figure 4. TGA plots of polymers **I-1** and **I-2** in nitrogen at a heating rate of 10 °C/min.

I-1 exhibiting its smectic LC phase, since it contained small bâtonnets that are the microstructures of this LC phase.[40,41] Thus, it was found that the tosylate ion, being incorporated as an organic counterion, is conducive to the thermotropic LC property of poly(pyridinium salt) because of the significant reduction of strong ionic interactions between positive and negative charges, which is in excellent agreement with the results of other ionic polymers.[27,42] Polymer **I-2** containing triflimide as a counterion also exhibited a T_m at 80 °C (at a heating rate of 10 °C/min), which is lower than that of polymer **I-1**. Similar to polymer **I-1**, the T_m of this polymer was reproducible and reversible, since it appeared at both the heating cycles of DSC thermograms (Figure 1b). It was also verified with TMA measurement (Figure 2b). Despite the presence of main-chain ionic character of each of these polymers, each of their T_m transitions exhibited a very low degree of supercooling in their cooling cycles. Although its LC-to-isotropic transition, T_i, was not distinctly detectable in the DSC thermogram because of the broadness of this endotherm, this transition was determined with the hot-stage PLM studies to be at about 180 °C, at which the disappearance of LC texture occurred completely. These results suggested that the triflimide as a counterion in polymer **I-2** not only decreased the T_m but also the T_i. Both of these transitions were well below their decomposition temperature at 316 °C. This decomposition temperature was also obtained at a heating rate of 10 °C/min in nitrogen by TGA measurement at which 5% weight loss of polymer **I-2** occurred (Figure 4). The polymer **I-2** had a broad range (100 °C) of LC phase. Figure 3b shows the photomicrograph of polymer **I-2** exhibiting the smectic LC phase, which also contains the bâtonnets texture indicative of this LC phase.[40,41] The X-ray diffraction patterns of polymer **I-2** were recorded at three different temperatures, but we were unable to make any conclusion regarding the nature of LC phase for this polymer. Although attempts were also made to align the LC phase in the presence of magnetic field, no success was made in the alignment of this viscous LC phase. The reason for both the low T_m and low T_i of polymer **I-2** originates partly from a recently reported crystal structure of 1-benzyl-2-ethyl-3-methyl imidazolium triflimide salt. The negative charge delocalization expected in this organic counterion extends only from the central nitrogen to the neighboring sulfur atoms and not to any great extent onto four sulfonyl oxygen atoms. The result of this partial delocalization through $p\pi-d\pi$ interactions is that the negative charge is significantly buried within the anion and shielded by four oxygen atoms and two terminal $-CF_3$ groups from Coulomb interactions with the neighboring cations. These reduced interactions, therefore, appear to be associated with the increased ion mobility and reduced lattice energy in the crystalline state.[43,44] Thus, it was reasonable to assume that the reduced ionic interactions between triflimide and 4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium) ions in polymer **I-2**, as are similar to the ionic salt (vide supra), provided a unique mechanism for its low T_m and low T_i. The thermal stability of polymer **I-2** was also much higher than that of polymer **I-1**. These results are in good agreement with the thermotropic LC properties of viologen polymers containing triflimide as a counterion.[27]

UV−vis and Photoluminescence Properties. Because both the polymers **I-1** and **I-2** contained 4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium) ions in the main chain that act as chromophores, they were examined for their optical properties both in solution and in the solid state. They displayed absorption maxima at 246 and 327 nm in methanol (ϵ = 32.6) in their UV−vis spectra. Polymer **I-1** had a broad absorption maximum at 257 nm in THF (ϵ = 7.6), but polymer **I-2** had absorption maxima at 250 and 329 nm in THF. All of these absorption maxima were indicative of closely spaced $\pi-\pi^*$ transitions common to aromatic rings. A model compound known as 1,2,4,6-tetraphenylpyridinium perchlorate exhibits essentially an identical absorption spectrum with a λ_{max} = 312 nm in ethanol. The absorption band of ortho-substituted pyridinium salt consists of two electronic transitions that are intramolecular charge transfer complexes of the 2,6- and the 4-substituent with the positively charged nitrogen center.[45] Thus, it was reasonable to state that the absorption bands of polymers **I-1** and **I-2** arose from the same electronic transitions as those in closely related pyridinium salts. The optical band gaps of these polymers (E_g's) as determined from the onset of wavelength in the UV−vis spectra in both methanol and THF were 3.38, 3.36, 3.44, and 3.33 eV. These band gaps were higher than those of other conjugated light-emitting polymers including poly(*p*-phenylenevinylene)s[12−15] but comparable with those of other related poly(pyridinium salt)s.[34] It appears that UV−vis spectra of these polymers were essentially independent of the structure of counterions and the polarity of solvents used.

The photoluminescence spectra of polymer **I-1** in both THF and methanol are shown in Figure 5. The emission peaks (λ_{em} = 359 nm) were evidently quite narrow in both the solvents with full width at half-maximum, fwhm, values ≈47 and 52 nm, respectively, all of which were indicative of an isolated emitting chromophore.[46] The characteristic sharpness of the emission peak indicated that the emitting chromophore in polymer **I-1** had a well-defined structure in both the solvents. The emission spectra of polymer **I-2 in** both THF and methanol (Figure 6) along with fwhm values ≈46 and 51 nm, respectively, were essentially identical to those of polymer **I-1.** These results suggested that the light emission occurred from the identical chromophore to that of polymer **I-1** and was independent of the nature of counterions.

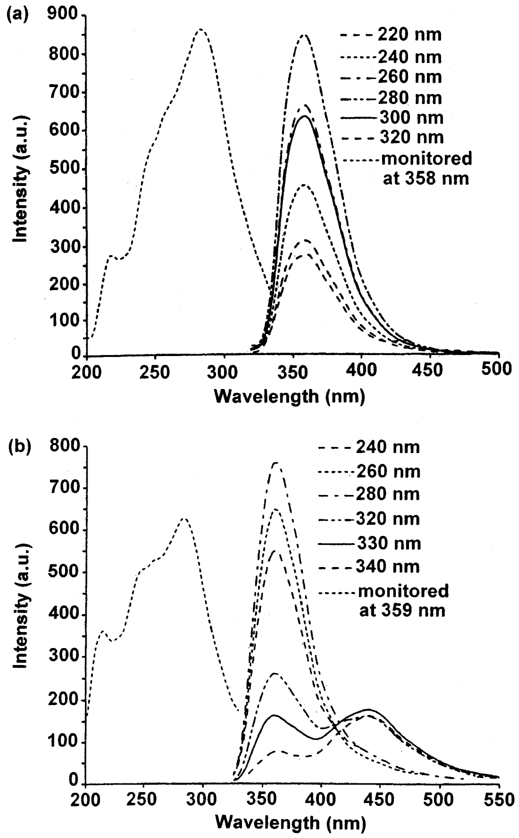


Figure 5. Emission spectra of polymer **I-1** at various excitation wavelengths: (a) in THF and (b) in methanol.

The films of polymers **I-1** and **I-2** were prepared from their respective solutions (THF or methanol) casting onto quartz plates. The solid-state emission spectra of polymer **I-1** cast from two different solvents are shown in Figure 7. In thin film, it showed a λ_{em} at 379 nm when cast from THF solution, but it showed a λ_{em} at 386 nm when cast from methanol solution. On going from solution to the thin film, there were only slightly bathochromic shift by 20 and 27 nm, respectively, in its λ_{em} values, when compared with those of solution spectra. These features strongly suggest that there existed less ordered structures in the solid-state films. The fwhm values of emission peaks in thin films of this polymer **I-1** were relatively broader when compared with those in solution spectra. Figure 8 depicts the thin film emission spectra of polymer **I-2** that are cast from THF and methanol. It exhibited a λ_{em} at 381 nm in THF-cast film at excitation wavelengths of 230−250 nm, but it exhibited a different broad emission peak (λ_{em} = 467 nm) at excitation wavelength of 320 nm. Thus, its λ_{em} values were bathochromically shifted by 22 and 108 nm, when compared with those of solution spectra. In contrast, its methanol-cast film exhibited a single λ_{em} at 467 nm for the excitation wavelengths of 300−380

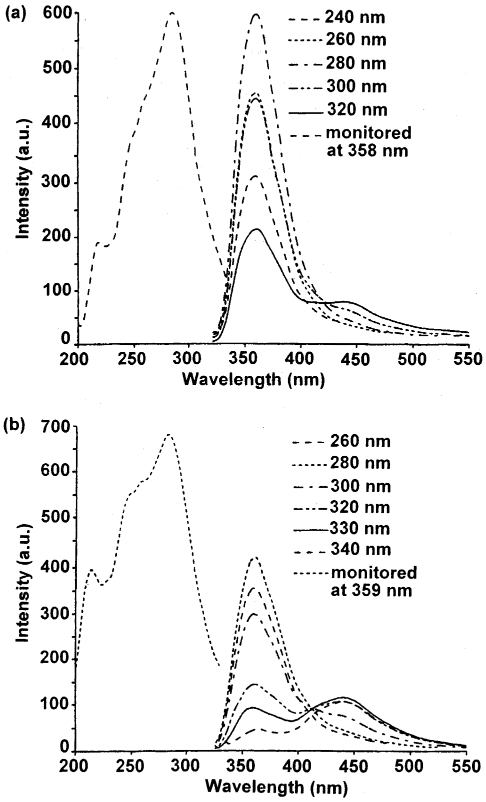


Figure 6. Emission spectra of polymer **I-2** at various excitation wavelengths: (a) in THF and (b) in methanol.

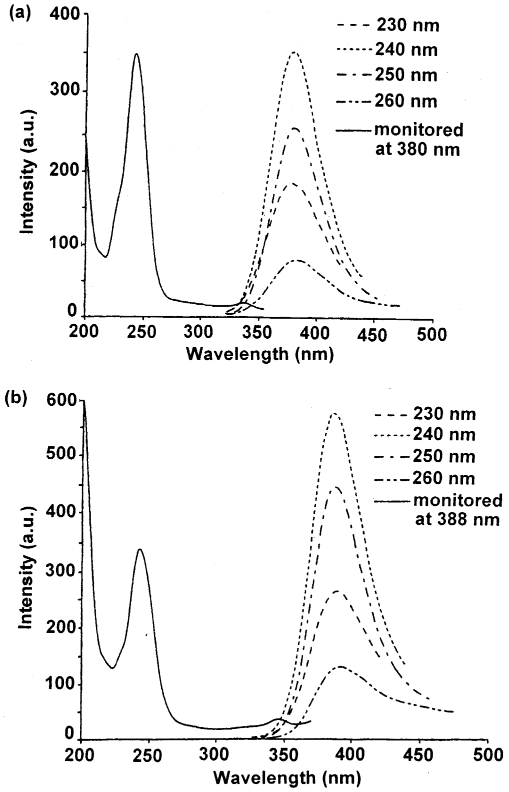


Figure 7. Emission spectra of polymer **I-1** in thin films at various excitation wavelengths: (a) cast from THF and (b) cast from methanol.

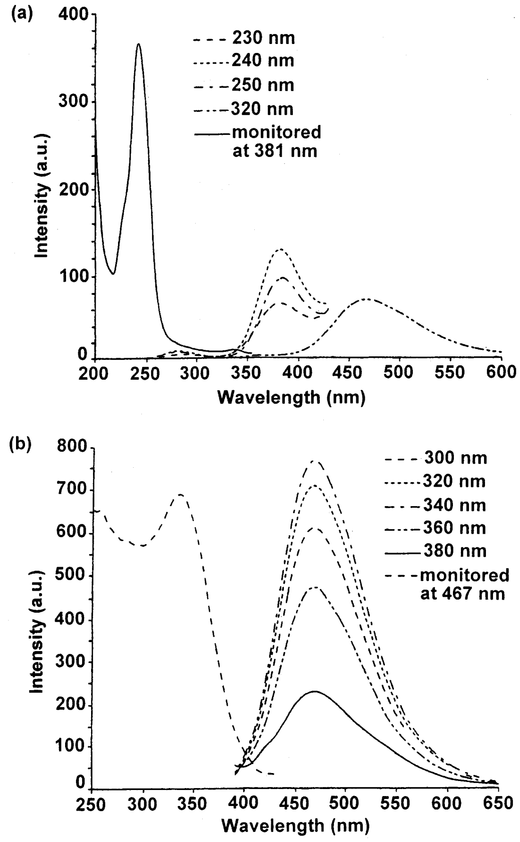


Figure 8. Emission spectra of polymer **I-2** in thin films at various excitation wavelengths: (a) cast from THF and (b) cast from methanol.

nm, which was insensitive to the excitation wavelength. Its λ_{em} value was red-shifted by 108 nm when compared with that of solution spectra. These results, when compared with those of polymer **I-1**, suggest that there were highly ordered structures in the solid-state films of polymer **I-2**, especially when film was cast from methanol. Both intra- and intermolecular $\pi-\pi$ interactions of chromophores are mainly responsible for these ordered structures, which in turn usually cause both to shift λ_{em} bathochromically and to lower the quantum yields of light-emitting polymers in the solid state in general.[47,48]

Conclusion

They are the first examples of poly(pyridinium salt)s with tosylate and triflimide counterions that exhibited thermotropic liquid-crystalline and light-emitting properties. The combination of thermotropic LC property, the ease of film formation, and photoluminescence makes these polymers interesting for optoelectronic applications such as polymer light-emitting devices, especially linearly polarized light emission. They are also ideal cationic polyelectrolytes for the preparation of multilayer assemblies with controlled morphologies at a molecular level by the sequential deposition technique with anionic polyelectrolytes.

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Supporting Information Available: IR (Figure S1), ^{1}H (Figure S2), and ^{13}C NMR spectra of polymer **I-2** (Figure S3); polyelectrolyte behavior of polymers **I-1** and **I-2** (Figure S4); and X-ray diffraction patterns of polymer **I-2** at different temperatures (Figure S5). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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