

Poly(pyridinium salt)s with Organic Counterions Derived from an Aromatic Diamine Containing Tetraoxyethylene Units Exhibiting Amphotropic Liquid-Crystalline and Photoluminescence Properties*

Pradip K. Bhowmik,¹ Haesook Han,¹ Alexi K. Nedeltchev,¹ Hari D. Mandal,² Jose A. Jimenez-Hernandez,² Patrick M. McGannon²

¹Department of Chemistry, University of Nevada at Las Vegas, Las Vegas, Nevada 89154

²Department of Biology and Chemistry, Texas A&M International University, Laredo, Texas 78041

Received 6 May 2009; accepted 23 October 2009

DOI 10.1002/app.31674

Published online 17 December 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Several poly(pyridinium salt)s containing various organic counterions and tetraoxyethylene units in their backbones were synthesized by either ring-transmutation polymerization reaction of 4,4'-(1,4-phenylene)-bis(2,6-diphenylpyrylium tosylate) with bis(2-(2-(4-aminophenoxy)ethoxy)ethyl) ether on heating in dimethyl sulfoxide or metathesis reaction of the tosylate polymer with the corresponding lithium or sodium salts in acetonitrile. Their chemical structures were determined by ¹H-NMR and ¹³C-NMR spectroscopy, and elemental analyses. Their number-average molecular weights and polydispersity indices were in the range of 34,000–52,000 and 1.14–1.38, respectively, as determined by gel permeation chromatography. They were characterized both for their

thermotropic and lyotropic liquid-crystalline properties by using differential scanning calorimetry and polarizing optical microscopy. As these polymers exhibited liquid-crystalline phase both in the melt and in solutions, they are classified as an amphotropic class of ionic polymers. Their light-emitting properties in a large number of organic solvents that ranged from nonpolar to polar solvents and in films cast from methanol and acetonitrile were also studied by using spectrofluorometry. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1197–1206, 2010

Key words: liquid-crystalline polymers; luminescence; polycondensation; thermogravimetric analysis; UV-vis spectroscopy

INTRODUCTION

Poly(pyridinium salt)s are an important class of macromolecules that contain ionic groups in their backbones, since they are suitable polymers for the construction of multilayer assemblies via electrostatic interactions. On the one hand, the polymers containing organic counterions that were prepared

from phenylated bis(pyrylium salt)s and aromatic diamines such as benzidine, 4,4'-oxydianiline and 2,6-diaminoanthracene exhibited lyotropic liquid-crystalline phase (LC) in various polar organic solvents. The solvents used for these polymers were dimethyl sulfoxide (DMSO), acetonitrile, and methanol. Their various critical concentrations (C^*) depended on the chemical structures of aromatic diamines. They also exhibited photoluminescence properties both in solutions and in the solid state.^{1,2} Similarly, polymers containing tosylate as counterions that were prepared by reacting 2-naphthylated bis(pyrylium salt)s with both 4,4'-oxydianiline and 4,4'-methylenedianiline showed lyotropic LC phase in methanol and DMSO. Their C^* values were dependent on the chemical structures of diamines, as expected. They also showed photoluminescence properties in these solvents.³ Polymers containing 2-naphthalenesulfonate as counterions that were prepared by reacting 4,4'-(1,4-phenylene)bis(2,6-diphenylpyrylium 2-naphthalenesulfonate) with both 4,4'-oxydianiline and 4,4'-methylenedianiline also showed lyotropic LC phase in these polar organic solvents at various C^* values. They also showed photoluminescence properties in these solvents.⁴ On

Additional Supporting Information may be found in the online version of this article

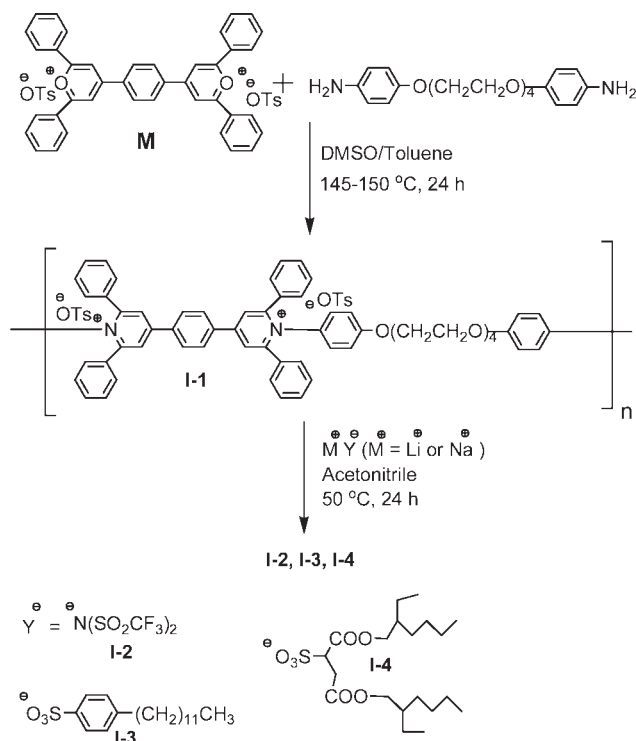
Correspondence to: P. K. Bhowmik (pradip.bhowmik@unlv.edu).

*This article is dedicated to Prof. Timothy C. K. Su with best wishes on the occasion of his 65th birthday.

Contract grant sponsors: University of Nevada Las Vegas (UNLV) for New Investigation Award (NIA), Planning Initiative Award (PIA), Applied Research Initiative (ARI) grants, Petroleum Research Fund (American Chemical Society), Texas A&M International University (TAMIU).

Contract grant sponsor: Research Corporation; contract grant number: CCSA# CC5589.

Contract grant sponsor: Welch Foundation; contract grant number: BS0040.



Scheme 1 Syntheses of ionic polymers.

the other hand, ionic polymers containing tosylate or triflimide counterions that were prepared from phenylated bis(pyrylium salt)s and 1,9-diaminononane or 1,12-diaminododecane exhibited both thermotropic LC and photoluminescence properties.^{5,6} Additionally, polymers consisting of these counterions that were prepared from phenylated bis(pyrylium salt)s and oxyalkylene diamines showed amphotropic LC⁷ and light-emitting properties.⁸ In this article, we describe the synthesis of a series of poly(pyridinium salt)s containing several organic counterions and four oxyethylene units in their backbones by ring-transmutation polymerization and metathesis reactions. They are characterized for both thermotropic and lyotropic LC properties in various organic solvents by using several experimental techniques. Their light-emitting properties in various organic solvents and in the solid state are also examined by using photoluminescence spectrometry. The general structures and designations of these ionic polymers, **I**, which were used in this study, are shown in Scheme 1.

EXPERIMENTAL

Monomer synthesis

4,4'-(1,4-phenylene)bis(2,6-diphenylpyrylium)ditosylate, **M**, was synthesized according to the known procedure.¹ The bis(2-(2-(4-aminophenoxy)ethoxy)ethyl) ether was also synthesized according to the

known procedure⁹ and obtained as a viscous liquid after the workup of the reaction mixture. It was then further purified by silica gel column chromatography using chloroform as an eluant. Anal. Calcd. for $\text{C}_{20}\text{H}_{28}\text{N}_2\text{O}_5$ (376.46): C, 63.81; H, 7.50; N, 7.44. Found: C, 63.46; H, 7.75; N, 7.82. The lithium triflimide (LiNTf_2), sodium dodecylbenzenesulfonate (NaDBS), and sodium dioctylsulfosuccinate (Na docusate) were also purchased from Sigma-Aldrich Chemical Company and used them without further purification for the metathesis reaction.

Polymer synthesis

Synthesis of polymer I-1

The bis(pyrylium salt) **M** was reacted with bis(2-(2-(4-aminophenoxy)ethoxy)ethyl) ether by ring-transmutation polymerization reaction¹ to yield polymer **I-1** that was carried out on heating in DMSO as shown in Scheme 1. Anal. Calcd. for $\text{C}_{74}\text{H}_{66}\text{N}_2\text{O}_{11}\text{S}_2$ (1223.48) (**I-1**): C, 72.65; H, 5.44; N, 2.29; S, 5.24. Found: C, 70.58; H, 5.51; N, 2.58; S, 4.41.

Synthesis of polymer I-2–I-4

All of them were prepared by the metathesis reaction of polymer **I-1** with the corresponding salts in a common organic solvent, such as acetonitrile.¹ Anal. Calcd. for $\text{C}_{64}\text{H}_{52}\text{N}_4\text{O}_{13}\text{F}_{12}\text{S}_4$ (1441.37) (**I-2**): C, 53.33; H, 3.64; N, 3.89; S, 8.90. Found: C, 51.02; H, 4.24; N, 3.99; S, 9.34. Anal. Calcd. for $\text{C}_{96}\text{H}_{110}\text{N}_2\text{O}_{11}\text{S}_2$ (1532.08) (**I-3**): C, 75.26; H, 7.24; N, 1.83; S, 4.19. Found: C, 72.98; H, 8.08; N, 1.77; S, 5.44. Anal. Calcd. for $\text{C}_{100}\text{H}_{126}\text{N}_2\text{O}_{19}\text{S}_2$ (1724.25) (**I-4**): C, 69.66; H, 7.37; N, 1.62; S, 3.72. Found: C, 67.79; H, 7.42; N, 1.79; S, 5.63.

Polymer characterization

The FTIR spectra of ionic polymers were recorded with a Shimadzu FTIR spectrometer using either their neat films on KBr pellets or methanol cast films directly on KBr windows. Their ¹H-NMR and ¹³C-NMR spectra of polymers were recorded with a VNMR 400 spectrometer with three RF channels operating at 400 and 100 MHz, respectively, in *d*₆-DMSO using TMS as an internal standard. Gel permeation chromatography (GPC) was performed for the synthesized polymers in DMSO at 40 °C with a flow rate 1.0 mL/min with a Waters 515 pump together with a Viscotek Model 301 Triple Detector Array that combines a laser refractometer, a differential viscometer, and a RALLS (right angle laser light scattering)/LALLS (low angle laser light scattering) at 7° detectors in a single instrument with fixed interdetector volumes and temperature control to 80 °C. Although conventional chromatographic

calibrations are not required for this type of GPC instrument, the pullulan standards of P-10 and P-50 from Polymer Standards Services were used for the instrument calibration. Separations were accomplished using ViscoGel I-MBHMW-3078 columns from Viscotek. A 100 μL of 0.2 wt % of polymer in DMSO containing 0.01 M LiBr was injected into the columns. Data analyses were performed using Viscotek TriSEC software. Phase transition temperatures were measured with a TA 2100 differential scanning calorimeter (DSC) under nitrogen flow at heating and cooling rates of $10^\circ\text{C}/\text{min}$. The temperature axis of the DSC thermogram was calibrated before use with the reference standard of high-purity indium and tin. Each of these polymers usually weighing 8–10 mg was used for this analysis. The thermogravimetric analysis (TGA) was performed with a TA 2100 instrument at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen. Both thermotropic and lyotropic LC properties of these polymers were studied by using a polarized optical microscope (POM, Nikon, Model Labophot 2) equipped with crossed polarizer and a hot stage. Samples of these ionene polymers for lyotropic properties were made by dissolving known amounts of polymers into known amounts of specific solvents and then occasionally shaken for several days for equilibration. Their UV-vis absorption spectra in spectrograde organic solvents were recorded with a Varian Cray 3 Bio UV-vis spectrophotometer at ambient temperature. Their photoluminescence spectra in solutions and solvent-cast thin films were recorded with a Perkin-Elmer LS 55 luminescence spectrometer with a xenon lamp light source. The solvent-cast films were prepared by placing the respective polymer solutions on quartz slides and allowed them to dry by evaporation at room temperature. Then these films were finally dried in vacuum oven to remove completely any residual solvents.

RESULTS AND DISCUSSION

Chemical structures

Figure 1 shows the FTIR spectrum of polymer I-4 recorded in thin film cast from methanol at room temperature that contains the following characteristics absorption bands: 3060 ($=\text{C}-\text{H}$ aromatic stretching), 2959, 2930, 2867 ($\text{C}-\text{H}$ aliphatic stretching), 1734 (ester carbonyl), 1621 ($\text{C}=\text{C}$ aromatic ring stretching), 1458 ($\text{C}-\text{H}$ aliphatic bending), 1152 ($\text{S}=\text{O}$ asymmetric stretching), 1035 ($\text{S}=\text{O}$ symmetric stretching), and 848, 763, and 702 cm^{-1} ($=\text{C}-\text{H}$ out-of-plane bending). The characteristic absorption bands of SO_3 group of DBS ion (both asymmetric and symmetric stretching) in polymer I-3 occurred at lower frequencies at 1026 and 1119 cm^{-1} than

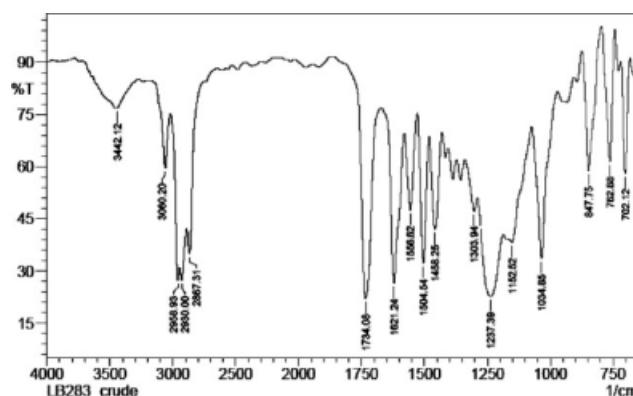


Figure 1 FTIR spectrum of polymer I-4 recorded in thin film cast from methanol on KBr window at room temperature.

those of the docusate ion in polymer I-4. In general, the symmetric bands of SO_3 group with organic cations occurred at lower frequencies than those with inorganic cations such as alkali metal ions. This phenomenon is attributed to the formation of contact ion pairs that polarize the $\text{S}-\text{O}$ dipoles by the electrostatic field of adjacent counterions.^{10,11} The lower frequencies of symmetric bands of SO_3 groups as well as NTf_2 in these ionic polymers clearly demonstrated that there were weak ion pair dipoles between the organic counteranions with the phenylated bipyridinium ions. These results are in excellent agreement with those of other ionic polymers reported in the literature.^{5,6,12}

In the ^{13}C -NMR spectrum of polymer I-1, the carbonyl resonance at ca. 187 ppm,¹³ which is attributable to a vinylous amide, was not detected in its spectrum (Supporting Information Figure S1) suggesting that the ring-transmutation polymerization reaction proceeded to completion under the experimental conditions used. The proton signals of vinylous amide and amino end groups were also not detected in its ^1H -NMR spectrum suggesting that it was of moderate molecular weight polymer. Additionally, its finger-nail creasable film could be easily cast from organic solvents suggestive of reasonably high molecular weight polymer. The ^1H - and ^{13}C -NMR spectra of polymers I-2 and I-3 (Supporting Information Figures S2–S3) along with their elemental analysis data also confirmed their chemical structures. The absence of tosylate proton signals in polymer I-2 (Supporting Information Figure S2) suggested that the exchange of tosylate ions in polymer I-1 with triflimide was effective in the metathesis reaction under the experimental protocols used for this polymer. The complete absence of aromatic protons as well as methyl proton signals of tosylate ions in polymer I-3 and appearance of aromatic protons at slightly different chemical shifts and different shapes when compared with tosylate aromatic

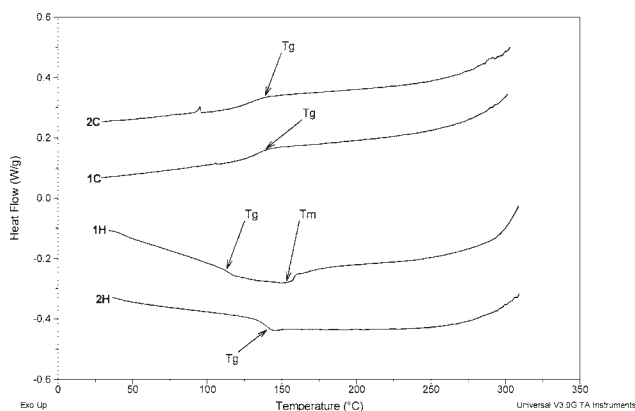


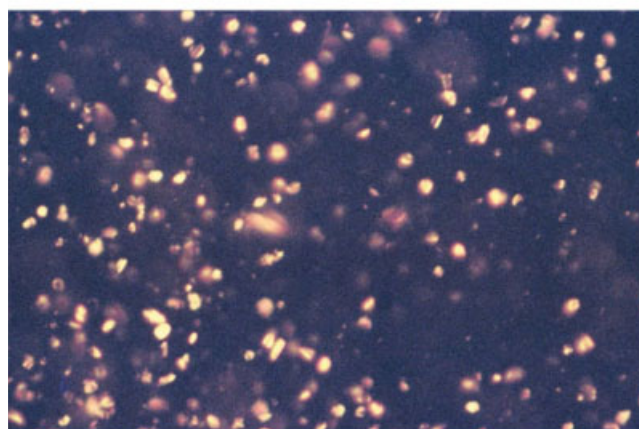
Figure 3 DSC thermograms of (a) polymer I-1 and (b) polymer I-2 obtained at heating and cooling rates of 10°C/min in nitrogen.

150°C, it formed very viscous melt exhibiting weakly birefringent texture (not shown) at this temperature. However, with further heating to a high temperature and on shearing this polymer, there was a development of highly birefringent texture as observed under the crossed polars indicative of its LC character [Fig. 4(a)]. This LC texture persisted up to its decomposition temperature at 325°C, as determined by TGA at a heating rate of 10°C/min in nitrogen (Fig. 5). In other words, the broad endotherm in the first heating cycle was related to overlapped transition of T_g and T_m of this polymer; and its T_i was neither detected in the DSC thermograms and nor could be determined on heating the polymer on the hot-stage of POM studies because of its decomposition at high temperatures.

Polymer I-2 showed a broad endotherm at low-temperature region and an indistinct, broad endotherm at high-temperature region in the first heating cycle. In the subsequent heating cycle, it exhibited a single T_g at 90°C and an exceedingly small endotherm at ca. 340°C. In the first and second cooling cycles, it exhibited a T_g at 84 and 75°C, respectively. However, on applying heat to this polymer to a temperature of ca. 60°C higher than its T_g and on shearing simultaneously, it formed a birefringent melt containing round objects suggesting its LC texture [Fig. 4(b)]. The high-temperature endotherm was related to LC-to-isotropic liquid transition (T_i) at 340°C as verified with POM studies, the temperature at which the disappearance of birefringent texture occurred. The broadness of both the endotherms of T_m in the first heating cycle and T_i in both the heating cycles was related to the low enthalpies for these transitions of this ionic polymer. The absence of T_m in the DSC thermogram in the second heating cycle was also related to the low enthalpy of melting, which was beyond the detection limit of DSC instrument used. Polymer I-2 had not only a broad temperature



(a)



(b)

Figure 4 Photomicrographs of (a) polymer I-1 taken at 220°C and (b) polymer I-2 taken at 170°C, respectively, under crossed polarizers exhibiting smectic LC phases (magnification $\times 400$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

range LC phase of ca. 190°C but also a high thermal stability of 386°C, as determined by TGA (Fig. 5). In fact, it had the highest thermal stability and polymer I-4 had the lowest thermal stability of 257°C (Fig. 5)

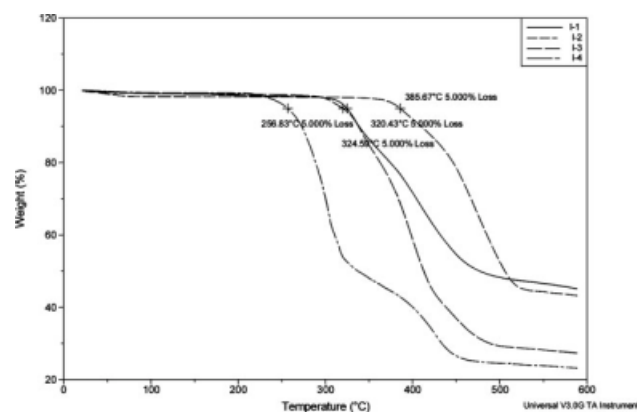


Figure 5 TGA plots of polymers I-1-I-4 obtained at a heating rate of 10°C/min in nitrogen.

among all the polymers in this series, as expected. All of these results are consistent with those reported earlier in the literature.^{5,6,8}

The features of DSC thermograms of polymers **I-3** and **I-4** were essentially similar in the sense that each of them showed an indistinct, broad endotherm in the first heating cycle. Each of them showed a single T_g in the second heating cycle. They were at 129°C and 67°C, respectively. In each of the cooling cycles, each of them showed a single T_g , which was slightly lower than that in the corresponding heating cycle. For example, the T_g values for these polymers in the second cooling cycles were at 128°C and 59°C, respectively (Supporting Information Figure S4). The POM studies suggested that they formed viscous melts at ca. 180°C and ca. 100°C, which were 52 and 41°C higher than the corresponding T_g values in the second heating cycles. Figure S5 (Supporting Information) showed the birefringence textures along with homeotropic alignment of black backgrounds recorded at 220°C and 200°C, respectively. The homeotropic alignments of the optical textures are presumably related to the spontaneous alignment promoted by the ionic species present in these polymers that act as a surface treatment agent. This phenomenon is quite common to many ionic LC compounds.^{14,15} However, on shearing the viscous melts of this class of ionic polymers, the development of birefringent textures occurred as observed under the crossed polars suggesting their LC properties. Furthermore, polymer **I-3** exhibited a T_i at 233°C as verified with POM studies and thus had a mesophase range of ca. 53°C. In contrast, polymer **I-4** exhibited LC texture up to its decomposition temperature, that is, no T_i . Note here that poly(pyridinium salt)s with the identical chemical structures but with BF_4^- as inorganic counterions, prepared from phenylated bis(pyrylium salt)s and aromatic diamines containing dioxyethylene and trioxyethylene units, do not exhibit thermotropic LC properties because of their thermal decomposition before melting transitions, although each of them contained short flexible units compared to tetraoxyethylene unit in the backbones as used in this study.¹⁶ Therefore, the combination of each of these organic counterions and tetraoxyethylene units in each of these ionic polymers is conducive to the formation of thermotropic LC phase without thermal decomposition. The single oxyethylene unit or a multiple thereof as the flexible units either in the main chain or in the side chain were used extensively in the field of thermotropic LC polymers that included polyesters^{17–19} and polyimides,^{9,20–22} among other polymers including ionic polymers,²³ to control the thermal transitions of these polymers for LC properties. The tetraoxyethylene units were also employed to develop photocrosslinkable nematic main-chain polymers

with high degree of polymerizations and relatively low isotropization temperatures. Interestingly enough, this class of elastomers resembled spider silk in their mechanical properties.²⁴ These flexible units were used to synthesize a series of unsaturated poly(ether ester amide)s for their good hydrophilicity, good solubility in various organic solvents, and good degradability.²⁵ In recent years, they were also employed to enhance the solubility of π -conjugated polymers and to fine-tuning the emission of visible light for the exploitation of optoelectronic devices. Additionally, they provide a significant ionic conductivity that can, in principle, be exploited for fabricating light-emitting electrochemical cells.^{26–30}

Lyotropic liquid-crystalline properties

The solubility of ionic polymers in various polar solvents having dielectric constants within the range of 32.6–48.9 was quite significant, as expected, that motivated us to study the lyotropic LC properties in these solvents. Similar to several poly(pyridinium salt)s that exhibit lyotropic LC phase in both protic and aprotic polar solvents,^{1–4,8} polymer **I-1** containing tosylate as counterions formed an isotropic solution at 30 wt % in methanol ($\epsilon = 32.6$) at room temperature. At an intermediate concentration of 40 wt %, which is known as C^* , it formed a biphasic solution wherein there existed an anisotropic (LC phase) and an isotropic phase when examined with a POM under crossed polarizers. However, at high concentration of 60 wt % of this polymer in this solvent, the development of lyotropic phase was not quite prominent presumably because of high viscosity of this solution. In contrast, it formed isotropic solutions only at high concentration up to 50 wt % in acetonitrile ($\epsilon = 37.5$) at room temperature. Like in acetonitrile, in DMSO ($\epsilon = 48.9$), it also had solubility as high as 39 wt % wherein there was no development of detectable birefringence textures suggestive of their isotropic solutions as verified with POM studies. Polymer **I-2** containing triflimide ion as counterions had relatively low solubility in methanol at room temperature, however, it exhibited a biphasic (birefringent and dark regions) solution at low concentration of 10 wt % in this solvent (Supporting Information Figure S6). In acetonitrile, it formed isotropic, biphasic and lyotropic solutions at 30, 40, and 50 wt %, respectively. Its solution properties in DMSO were essentially identical to those of polymer **I-1**, that is, it formed isotropic solutions as high as 39 wt % in this solvent. Polymer **I-3** containing DBS as counterions formed isotropic, biphasic, and lyotropic solutions (Supporting Information Figure S6) at 29, 40, and 51 wt %, respectively, in methanol. Similarly, its C^* and concentration for the formation of biphasic and lyotropic solutions were 30 and

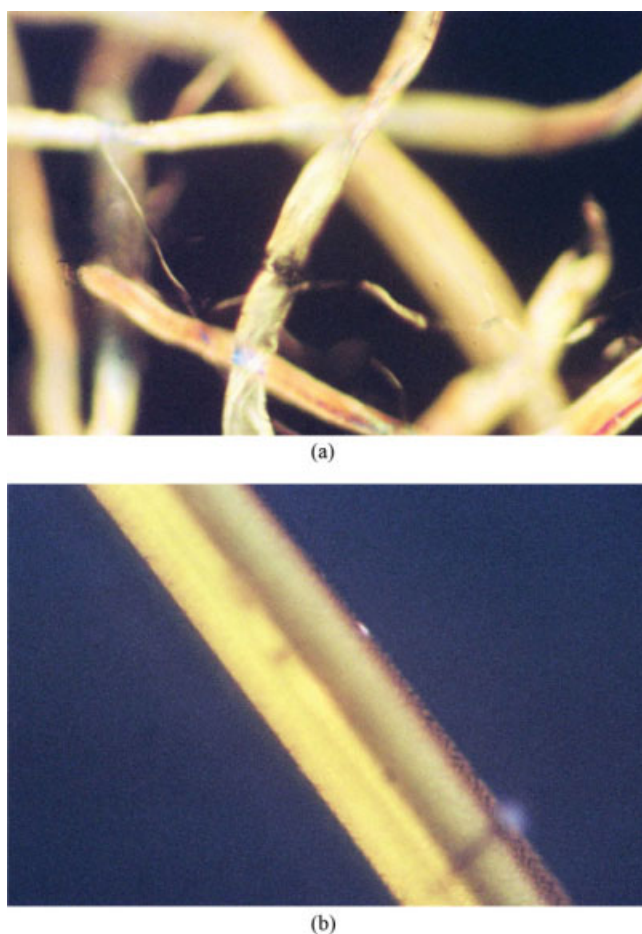


Figure 6 Photomicrographs taken at room temperature of: (a) polymer I-4 at 70 wt % in CH₃OH and (b) a hand-drawn fiber obtained from polymer I-4 at 62 wt % in acetonitrile under crossed polarizers exhibiting lyotropic LC phases, respectively (magnification $\times 400$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

40 wt %, respectively, in acetonitrile; and those were 30 and 50 wt %, respectively, in DMSO. Polymer I-4 containing docusate as counterions formed biphasic solutions (ribbon-shaped birefringence) over a broad range of concentrations of ca. 30–70 wt % in methanol [Fig. 6(a)]. Note here that these birefringence textures of biphasic solutions retained for a few days or more on simple evaporation of solvent at room temperature.^{31–35} In acetonitrile, it also exhibited similar biphasic solutions at ca. 30 and 40 wt % with identical textures to those in methanol. Interestingly enough, fibers were easily drawn from its 50 or 60 wt % in acetonitrile by gently pulling with a pair of tweezers by hand [Fig. 6(b)] and examined with a POM under crossed polarizers, revealing the birefringence textures and orientations inside them. In DMSO, it formed an isotropic solution at a concentration up to 40 wt %; and its biphasic solution appeared at ca. 50 wt % in this solvent. However, unlike polymer I-3, its fully grown lyotropic phase

in any of these solvents could not be determined because of its high solution viscosities. Note here that the difficulty in the preparation of thin films from highly viscous solutions of ionic polymers hindered the development LC textures, since the well-developed textures in LC polymers usually occur in thin films under crossed polarizers.⁸ Their high solubility in various polar solvents was related to the high solvophilic effects of these solvents with the pyridinium ions associated with various organic counterions in conjunction with four oxyethylene units present along the backbones of these polymers.

Photoluminescence properties

As each of the ionic polymers contained organic counterions, which were associated with phenylated pyridinium moieties, and four oxyethylene units in their backbones, they had good solubility in various polar organic solvents. Polymer I-3 containing DBS as counterions had also sufficient solubility in low polar solvents such as chloroform ($\epsilon = 4.9$), tetrahydrofuran ($\epsilon = 7.6$), and acetone ($\epsilon = 20.6$). Their solubility in various organic solvents allowed us to examine the optical properties that included UV–vis absorption spectra and photoluminescence properties in their solutions as well as in their thin-film states cast from various solvents. For example, polymer I-3 showed a λ_{max} at 330, 325, 330, 330, 335, and 340 nm in chloroform, tetrahydrofuran, acetone, methanol, acetonitrile, and DMSO, respectively (Supporting Information Figure S7). The bathochromic shift in its λ_{max} values with the increase in relatively low polar solvent to high polar solvent suggested that all of these absorption maxima were indicative of closely spaced π – π^* transitions common to aromatic rings. A model compound what is known as 1,2,4,6-tetraphenylpyridinium perchlorate exhibits essentially an identical absorption spectrum with a $\lambda_{\text{max}} = 312$ 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.³⁶ Thus, it was reasonable to state that the absorption bands for all these polymers arose from the identical electronic transitions as those in closely related pyridinium salts. The optical band gaps of polymer I-3 (E_g values) as determined from the onset of wavelength in the UV–vis spectra in these various solvents were in the narrow range of 3.27–3.35 eV. These band gaps were higher than those of a class of π -conjugated light-emitting polymers including poly(*p*-phenylenevinylene)s,^{37,38} but comparable with those of other related poly(pyridinium salt)s.^{6,39}

Table II summarizes the optical properties of ionic polymers in various organic solvents and solvent-

TABLE II
Optical Properties of Ionic Polymers in Various Organic Solvents and Solvent-Cast Films

Polymer	I-1	I-2	I-3	I-4
PL λ_{em} CHCl ₃ (nm)	– ^a	– ^a	525 (330) ^b	525 (330) ^b
PL λ_{em} THF (nm)	– ^a	532 (340) ^b	528 (330) ^b	517 (340) ^b
PL λ_{em} Acetone (nm)	544 (340) ^b	– ^a	538 (350) ^b	540 (340) ^b
PL λ_{em} CH ₃ OH (nm)	539 (390) ^b	540 ^c (340) ^b	542 (340) ^b	539 (340) ^b
PL λ_{em} CH ₃ CN (nm)	544 (360) ^b	547 (340) ^b	545 (360) ^b	546 (340) ^b
PL λ_{em} film from CH ₃ OH (nm)	505 (340) ^b	481 (330) ^b	475 (340) ^b	484 (325) ^b
PL λ_{em} film from CH ₃ CN (nm)	497 (340) ^b	499 (340) ^b	499 (340) ^b	477 (325) ^b

^a Not measured.

^b The number in the parenthesis indicates the excitation wavelength used for the measurement.

^c λ_{em} at 367 nm was also observed when excited at 265 nm wavelength.

cast thin films. Figure 7 shows the emission spectra of these polymers in acetonitrile at various excitation wavelengths of light, each of which consists of a broad, distinct λ_{em} peak with indistinct vibrational structures. These spectra are the representative to those in other solvents (Supporting Information Figures S8 and S9). Their λ_{em} peaks were also slightly dependent on the nature of counterions and in the narrow range of 544–547 nm, when excited at various excitation wavelengths of light, in a relatively polar aprotic solvent like acetonitrile. Thus, it appeared that each of them showed a bathochromic shift to a small extent in this solvent when compared with those in either tetrahydrofuran or acetone. The fwhm value for each of the emission spectra is also quite broad like that in tetrahydrofuran or acetone. Like in methanol, the polymer I-2 also emitted UV light at λ_{em} peak at 367 nm (shoulder peak at 433 nm) when excited at 265 nm wavelength of light in acetonitrile with a narrow fwhm value. The excitation spectra of polymers I-1 and I-3 showed essentially identical features in the sense that each of them exhibited three λ_{ex} peaks at 250, 265, and 360 nm, when monitored at 550 nm wavelength of light (not shown). The excitation spectrum of polymer I-2 consisted of four λ_{ex} peaks at 246, 267, 306, and 338 nm, when monitored at 545 nm wavelength of light, but that of polymer I-4 consisted of two λ_{ex} peaks at 298 and 344 nm when monitored at identical wavelength of light (not shown).

The films of these polymers were prepared from their respective solutions (methanol or acetonitrile) casting onto quartz plates. Their solid-state emission spectra cast from two different solvents were shown in Figure 8. In thin films when cast from methanol solutions, all of these polymers showed a broad λ_{em} peak in their emission spectra with the complete loss of vibrational fine structures at 505, 481, 475, and 484 nm when excited at 340, 330, 340, and 325 nm wavelengths of light [Fig. 8(a)]. Their excitation

spectra showed a major λ_{ex} peak with vibrational fine structures in the broad range of 325–338 nm when monitored at the wavelengths of their λ_{em} peak values. On changing from solutions to the thin films, they showed large hypsochromic shifts of 37, 60, 67, and 54 nm in their λ_{em} values, when compared with those of solutions spectra. Similarly, when their films were cast from another solvent acetonitrile, they also showed a broad λ_{em} peak in their emission spectra with the complete loss of vibrational fine structures at 497, 499, 499, and 477 nm when excited at identical wavelength of 340 nm light [Fig. 8(b)]. Their excitation spectra showed a major λ_{ex} peak with occasional vibrational fine structures in the narrow range of 326–336 nm when monitored at the wavelengths of their λ_{em} peak values. On changing from solutions to the thin films, they showed large hypsochromic shifts of 47, 48, 48, and 69 nm in their λ_{em} values, when compared with

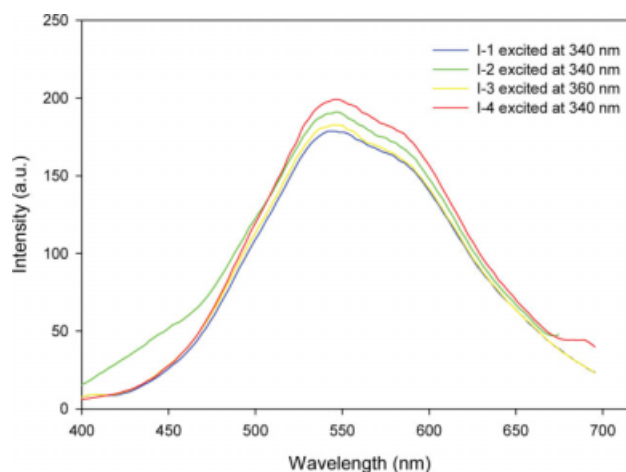


Figure 7 Emission spectra of polymers I-1–I-4 in acetonitrile at various excitation wavelengths. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

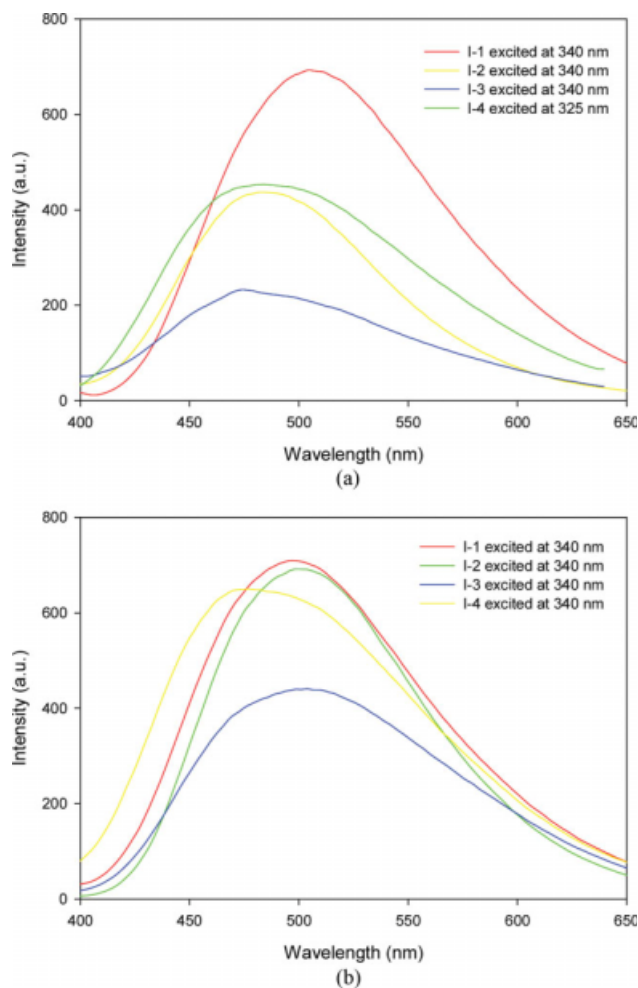


Figure 8 Emission spectra of polymers **I-1–I-4** in thin films: (a) cast from methanol at various excitation wavelengths and (b) cast from acetonitrile at identical excitation wavelength, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

those of their solutions spectra. The fwhm values of emission spectra in thin films of these polymers cast from both methanol and acetonitrile were relatively narrower when compared with those in their solutions spectra in these solvents. These features strongly suggest that there existed less ordered structures in the solid-state morphology of these ionic polymers. Note here that both intramolecular and intermolecular π – π interactions of chromophores of polymers are mainly responsible for the ordered structures, which in turn usually cause both to shift λ_{em} bathochromically to a great extent as high as 100 nm or higher and to lower the quantum yields of light-emitting polymers in the solid state in general.^{40,41} These π – π interactions of chromophores were essentially minima in this class of poly(pyridinium salt)s containing tetraoxyethylene units. The light emission for each of these polymers occurred

in the solid state in the blue region of the visible light.

CONCLUSIONS

Several poly(pyridinium salt)s with organic counterions (OTs, NTf₂, DBS, and docusate) were prepared by either the ring-transmutation polymerization of phenylated bis(pyrylium tosylate) salt with bis(2-(2-(4-aminophenoxy)ethoxy)ethyl) ether in DMSO or the metathesis reaction of the tosylate polymer with the corresponding lithium or sodium salts in acetonitrile. Their intrinsic viscosities and weight-average molecular weights were in the range of 0.09–0.15 dL/g and 42,000–71,000, respectively, as determined by GPC. They were characterized for their both thermotropic and lyotropic liquid-crystalline properties with various experimental techniques. Polymers **I-1** and **I-4** exhibited smectic liquid-crystalline phase at relatively low temperatures that persisted up to their decomposition temperatures. Polymers **I-2** and **I-3** had not only low T_m value but also low T_i value thus exhibiting a broad temperature range of LC phase. Polymers **I-2** and **I-4** had the highest and lowest thermal stability, respectively, in the series of these ionic polymers. Additionally, the C^* values of polymer **I-2** in acetonitrile and polymer **I-3** in methanol were essentially identical, which were 40 wt % in these polar solvents. They are the novel members of a class of poly(pyridinium salt)s with various organic counterions that exhibited both lyotropic and thermotropic liquid-crystalline properties, which can be classified as amphotropic polymers. Although the literature is replete with many lyotropic (solvent induced) and many thermotropic (heat induced) liquid-crystalline polymers,⁴² relatively few amphotropic liquid-crystalline polymers both neutral and ionic polymers exist to date.^{7,8,31,43–46}

All of them exhibited light-emitting properties both in various organic solvents as well as in the solid state. For example, polymer **I-1** emitted light of wavelengths 542 nm in methanol and 544 nm in acetonitrile solutions. In its thin films cast from both methanol and acetonitrile, the wavelengths of light emission were shifted hypsochromically to 505 and 497 nm, respectively, because of the less ordered structures in the solid state.

The combination of thermotropic and lyotropic liquid-crystalline properties, the ease of film formation, and photoluminescence makes this class of ionic polymers interesting for practical applications. They are also ideal cationic polymers for the preparation of multilayer assemblies with controlled morphologies at a molecular level by the sequential deposition technique with anionic polymers.

A.K.N. acknowledges the Graduate College (UNLV) for providing him a Nevada Stars Graduate Assistantship for the period of 2006–2008.

References

1. Bhowmik, P. K.; Burchett, R. A.; Han, H.; Cebe, J. J. *Macromolecules* 2001, 34, 7579.
2. Bhowmik, P. K.; Han, H.; Nedeltchev, A. K. *Polymer* 2006, 47, 8281.
3. Bhowmik, P. K.; Burchett, R. A.; Han, H.; Cebe, J. J. *J Polym Sci Part A: Polym Chem* 2001, 39, 2710.
4. Bhowmik, P. K.; Burchett, R. A.; Han, H.; Cebe, J. J. *J Polym Sci* 2002, 43, 1953.
5. Bhowmik, P. K.; Han, H.; Cebe, J. J.; Nedeltchev, I. K.; Kang, S.-W.; Kumar, S. *Macromolecules* 2004, 37, 2688.
6. Bhowmik, P. K.; Han, H.; Nedeltchev, A. K. *J Polym Sci Part A: Polym Chem* 2006, 44, 1028.
7. Tschierske, C. *Curr Opin Colloid Interface Sci* 2002, 7, 355.
8. Bhowmik, P. K.; Kamatam, S.; Han, H.; Nedeltchev, A. K. *Polymer* 2008, 49, 1748.
9. Feld, W. A.; Ramalingam, B.; Harris, F. W. *J Polym Sci Polym Chem Ed* 1983, 21, 319.
10. Cable, K. M.; Mauritz, K. A.; Moore, R. B. *J Polym Sci Part A: Polym Chem* 1995, 33, 1065.
11. Sander, B.; Tübke, J.; Wartewig, S.; Shaskov, S. *Solid State Ionics* 1996, 83, 87.
12. Bhowmik, P. K.; Han, H.; Cebe, J. J.; Burchett, R. A.; Sarker, A. M. *J Polym Sci Part A: Polym Chem* 2002, 40, 659.
13. Katritzky, A. R.; Brownlee, R. T. C.; Musumarra, G. *Tetrahedron* 1980, 36, 1643.
14. Binnemans, K. *Chem Rev* 2005, 105, 4148.
15. Godinho, M. H.; Cruz, C.; Teixeira, P. I. C.; Ferreira, A. J.; Costa, C.; Kulkarni, P. S.; Afonso, C. A. M. *Liq Cryst* 2008, 35, 103.
16. Harris, F. W.; Chuang, K. C.; Huang, S. A. X.; Janimak, J. J.; Cheng, S. Z. D. *Polymer* 1994, 35, 4940.
17. Ober, C.; Lenz, R. W.; Galli, G.; Chiellini, E. *Macromolecules* 1983, 16, 1034.
18. Bhowmik, P. K.; Garay, R. O.; Lenz, R. W. *Makromol Chem* 1991, 192, 415.
19. Lenz, R. W.; Furukawa, A.; Bhowmik, P. K.; Garay, R. O.; Majnusz, J. *Polymer* 1991, 32, 1703.
20. Kricheldorf, H. R. *Adv Polym Sci* 1999, 141, 83.
21. Eastmond, G. C.; Paprotny, J. *Polymer* 2002, 43, 3455.
22. Costa, G.; Eastmond, G. C.; Fairclough, J. P. A.; Paprotny, J.; Ryan, A. J.; Stagnaro, P. *Macromolecules* 2008, 41, 1034.
23. Han, H.; Vantine, P. R.; Nedeltchev, A. K.; Bhowmik, P. K. *J Polym Sci Part A: Polym Chem* 2006, 44, 1541.
24. Krause, S.; Dersch, R.; Wendorff, J. H.; Finkelmann, H. *Macromol Rapid Commun* 2007, 28, 2062.
25. Wang, L.; Wang, Y.; Cao, D. *J Macromol Sci Part A: Pure Appl Chem* 2009, 46, 282.
26. Pei, Q.; Yang, Y. *J Am Chem Soc* 1996, 118, 7416.
27. Yang, C.; He, G.; Wang, R.; Li, Y. *Mol Cryst Liq Cryst* 1999, 337, 473.
28. Cacialli, F.; Friend, R. H.; Feast, W. J.; Lovenich, P. W. *Chem Commun* 2001, 1778.
29. Mihara, T.; Yada, T.; Koide, N. *Mol Cryst Liq Cryst* 2004, 411, 421.
30. Hargadon, M. T.; Davey, E. A.; McIntyre, T. B.; Gnanamgari, D.; Wynne, C. M.; Swift, R. C.; Zimbalist, J. R.; Fredericks, B. L.; Nicastro, A. J.; Goodson, F. E. *Macromolecules* 2008, 41, 741.
31. Bhowmik, P. K.; Han, H.; Nedeltchev, I. K. *J Polym Sci Part A: Polym Chem* 2002, 40, 2015.
32. Bhowmik, P. K.; Molla, A. H.; Han, H.; Gangoda, M. E.; Bose, R. N. *Macromolecules* 1998, 31, 621.
33. Bhowmik, P. K.; Han, H.; Basheer, R. A. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC: Boca Raton, FL, 1996; Vol. 5, p 3741.
34. Bhowmik, P. K.; Han, H. *J Polym Sci Part A: Polym Chem* 1995, 33, 1745.
35. Han, H.; Bhowmik, P. K. *Trends Polym Sci* 1995, 3, 199.
36. Makoswski, M. P.; Mattice, W. L. *Polymer* 1993, 34, 1606.
37. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew Chem Int Ed* 1998, 37, 402.
38. Mitschke, U.; Bäuerle, P. *J Mater Chem* 2000, 10, 1471.
39. Spiliopoulos, I. K.; Mikroyannidis, J. A. *J Polym Sci Part A: Polym Chem* 2001, 39, 2454.
40. Sarker, A. M.; Strehmel, B.; Neckers, D. C. *Macromolecules* 1999, 32, 7409.
41. Gettinger, C.; Heeger, A. J.; Drake, J.; Pine, D. *J Chem Phys* 1994, 101, 1673.
42. Donald, A. M.; Windle, A. H. *Liquid Crystalline Polymers*; Cambridge University: Cambridge, 1999; pp 1–310.
43. Aharoni, S. M. *J Polym Sci: Polym Phys Ed* 1980, 18, 1303.
44. Kaeriyama, K.; Kouyama, S.; Sekita, M.; Nakayama, T.; Tsukahara, Y. *Macromol Rapid Commun* 1999, 20, 50.
45. Mruk, R.; Prehl, S.; Zentel, R. *Macromol Chem Phys* 2004, 205, 2169.
46. Choi, K.; Mruk, R.; Moussa, A.; Jonas, A. M.; Zentel, R. *Macromolecules* 2005, 38, 9124.