

Synthesis and characterization of poly(pyridinium salt)s with anthracene moieties exhibiting both lyotropic liquid-crystalline and UV light-emitting properties

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This article is dedicated to Professor Robert W. Lenz with best wishes on the occasion of his 80th birthday.

Abstract

Two poly(pyridinium salt)s with anthracene moieties in the main chain as well as tosylate and triflimide as counterions were prepared by either the ring-transmutation polymerization of phenylated bis(pyrylium tosylate) salt with 2,6-diaminoanthracene in dimethyl sulfoxide or the metathesis reaction of the corresponding tosylate polymer with lithium triflimide in acetonitrile. They were characterized for their lyotropic liquid-crystalline and UV light-emitting properties, with various experimental techniques. These ionic, conjugated anthracene polymers are the recent addition to the class of UV light-emitting polymers, since they emit UV light both in solution and in the solid state.

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1. Introduction

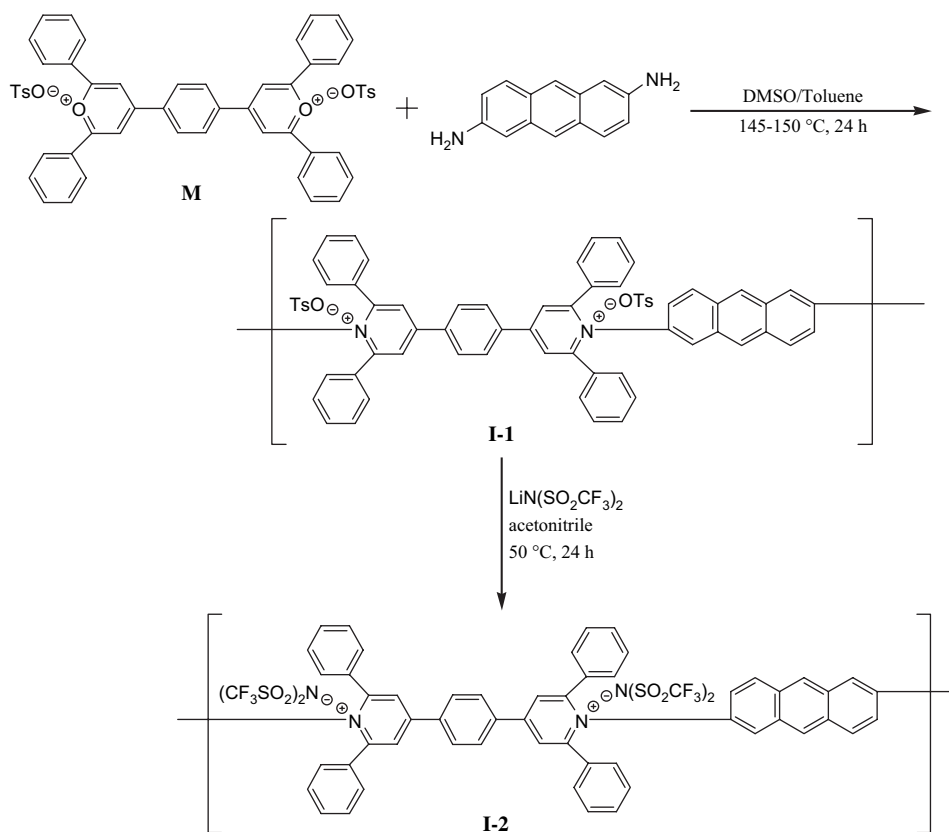
Since the first report of luminescence in poly(*p*-phenylenevinylene) (PPV) [1] in 1990, there is an ever-increasing interest in the development of π -conjugated polymers, especially in the development of high-efficiency, long lifetime, and good color-purity light-emitting polymers (LEPs). They can be used successfully for a wide variety of other optoelectronic applications such as photovoltaic devices, and field-effect transistors. They typically include PPV, poly(*p*-phenyleneethynylene) (PPE), poly(*p*-phenylene) (PPP), ladder poly(*p*-phenylene) (LPPP), poly(fluorene) (PF), and poly(thiophene) (PT), poly(pyrrole) (PP), and their derivatives, among others [2–6]. Anthracene polymers having extended π -conjugation are also of considerable interest for photoluminescence and electroluminescent properties [7,8]. However, the synthesis of such polymers is, often, complicated by their insolubility in the chosen polymerization reaction media. In many cases,

synthesis via precursor polymers is a very useful and successful method [9–12]. In this method, generally, a readily soluble precursor polymer is synthesized which on heating is converted into the insoluble target polymer. By using this popular method, many anthracene polymers can be prepared that include polyamides, polyesters, poly(anthracene-2,6-diyl) and its copolymer with *p*-phenylene units, among others [8,13–15]. Anthracene containing polyimides are typically prepared by the polycondensation reaction of various aromatic dianhydrides with 9,10-bis(*p*-aminophenyl)anthracene by a two-stage procedure involving low-temperature polycondensation reaction [16] in *N*-methylpyrrolidone followed by thermal imidization of the cast films of polyamic acids at 300–320 °C in vacuum for 1 or 2 h. Many anthracene polymers and their copolymers can also be prepared by the coupling reactions, including Yamamoto and Suzuki reactions, in the presence of organometallic catalysts [17–20].

In this article, we describe the synthesis of two new cationic polymers—poly(pyridinium salt)s—containing bulky 2,6-anthracene moieties in the polymer backbone as well as organic counterions, such as tosylate and triflimide ions, by

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Scheme 1. Preparation of poly(pyridinium salt)s with tosylate and triflimide counterions.

ring-transmutation polymerization reaction [21–27] and the characterization of their lyotropic liquid-crystalline (LC) properties in polar organic solvents. 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 anthracene moieties in the main chain that exhibit lyotropic LC properties in various organic solvents. They also emit UV light both in solution and in the solid state. On the one hand, anthracene polymers of suitable architectures not only possess good film-forming properties and good thermal stability but also exhibit light emission with high photoluminescence (PL) and electroluminescence (EL) efficiencies [7,8]. On the other hand, water-soluble, π -conjugated polyelectrolytes [28–36] of both cationic and anionic types are attractive sensor materials [37–46], because their optoelectronic properties can be significantly modified by very minor perturbations of the environmental stimuli. There exist amplification mechanisms by a collective response of the repeating units in the macromolecules. Therefore, the synthesis and characterization of both lyotropic LC and light-emitting properties of poly(pyridinium salt)s with 2,6-anthracene moieties by using a variety of experimental techniques are of significant interest for the development of new cationic polyelectrolytes. The techniques used for characterization include solution viscosity, elemental analysis, Fourier transform infrared (FTIR) spectroscopy, Fourier transform nuclear magnetic resonance (FT-NMR), and polarizing optical microscopy (POM). Their photoluminescence

properties in the UV region of light both in solutions of polar solvents and in the solid state are also included.

2. Experimental section

2.1. Monomer synthesis

The 4,4'-(1,4-phenylene)bis(2,6-diphenylpyridinium)ditosylate, **M**, was synthesized by the modification of a procedure by which the corresponding bis(tetrafluoroborate) salt was prepared [27]. In this procedure, terephthalaldehyde was condensed with more than 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 [25]. Its purity was also checked by ¹H 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, CH₃). Anal. calcd for C₅₄H₄₂O₈S₂: 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 in quite agreement with the theoretical values ($C/O = 5.06$, $C/S = 10.12$, and $S/O = 0.50$) [47].

The 2,6-diaminoanthracene was prepared by the reduction reaction of 2,6-aminoanthraquinone with zinc in alkaline medium in accordance with the previously reported procedure [13]. Anal. calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.34; H, 6.19; N, 13.42. It showed a sharp melting endotherm ($\Delta H = 10.6$ kJ/mol) at peak maximum of 253 °C obtained at a heating rate of 10 °C/min in nitrogen followed by immediate decomposition (mp = 230 °C decomposed) [13].

2.2. Synthesis of polymer I-1

The bis(pyrylium) salt **M** was polymerized with 2,6-diaminoanthracene by ring-transmutation polymerization reaction [21–27] to yield polymer **I-1** that was carried out on heating in dimethyl sulfoxide (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}) 3055, 1614, 1596, 1548, 1493, 1446, 1393, 1357, 1180, 1119, 1032, 1010, 814, 761, 698, 679, 566. Anal. calcd for $C_{68}H_{50}N_2O_6S_2$ (**I-1**): C, 77.40; H, 4.78; N, 2.65; S, 6.08. Found: C, 76.81; H, 5.34; N, 2.73; S, 5.18.

2.3. 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 DMSO [21,22]. The procedure that was employed is described as follows. Three grams (2.84 mmol) of polymer **I-1** was dissolved in 50 mL of DMSO on gentle warming. To this solution of this polymer, 50 mL of DMSO solution of lithium triflimide (3.4 g, 11.8 mmol) was added dropwise on stirring. The resulting solution was kept at 50 °C overnight with stirring. After removing DMSO 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 vacuum at 50 °C for 48 h and weighed to give 3.2 g (2.51 mmol) of polymer **I-2** (yield 88%). Anal. calcd for $C_{58}H_{36}N_4O_8F_{12}S_4$ (**I-2**): C, 54.72; H, 2.85; N, 4.40; S, 10.07. Found: C, 59.84; H, 3.37; N, 4.28; S, 8.19.

2.4. Polymer characterization

The FTIR spectra of polymers were recorded with a Nicolet FTIR analyzer with their neat films on KBr pellets. Their ^1H and ^{13}C NMR spectra were recorded with a Bruker AM 400 spectrometer with three radiofrequency channels operating at 400 and 100 MHz, respectively, in d_6 -DMSO using tetramethylsilane 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. Solutions of these ionic polymers for the study of lyotropic properties were prepared by mixing known amounts of polymer and a specific solvent, such as methanol, DMSO and acetonitrile, and then shaking for a period of 7 d for equilibration. The polarizing optical microscopic (POM) studies were performed with a polarizing light microscope (Nikon, model Labophot 2) equipped with crossed polarizers and a hot stage. 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.

3. Results and discussion

3.1. Chemical structures

The FTIR (not shown), ^1H and ^{13}C NMR spectra of polymer **I-1** in d_6 -DMSO (Fig. 1) are consistent with its proposed structure. Furthermore, its ^{13}C NMR spectrum contains only aromatic carbon signals between 125 and 157 ppm. The carbonyl resonance at ca. 187 ppm, which is attributable to a vinylogous amide [48], was not detected suggesting that the ring-transmutation polymerization reaction proceeded to completion under the experimental protocols used. The proton signals of vinylogous amide and amino end groups were also not detected in its ^1H NMR spectrum. The FTIR spectrum of polymer **I-2** at room temperature on KBr pellets contains the following characteristic absorption bands in addition to other peaks: 3057, 2922 ($=\text{C}-\text{H}$ aromatic stretching), 1683, 1614 ($\text{C}=\text{C}$ aromatic ring stretching), 1351 ($\text{C}-\text{F}$ stretching), 1193 ($\text{H}_2\text{C}-\text{N}^+$), 1133 ($\text{S}=\text{O}$ asymmetric stretching), 1057 ($\text{S}=\text{O}$ symmetric stretching), and 779 cm^{-1} ($=\text{C}-\text{H}$ out-of-plane bending). The ^1H and ^{13}C NMR spectra of polymer **I-2** in d_6 -DMSO (Fig. 2) are consistent with its proposed structure. The absence of tosylate proton signals suggested that the exchange of tosylate ion with triflimide in polymer **I-2** was effective in the metathesis reaction under the experimental conditions used.

3.2. Dilute solution properties

Because of the presence of 4,4'-(1,4-phenylene)bis(2,6-diphenylpyridinium) ions along the backbone of the polymer chain polymer **I-1** showed a polyelectrolyte behavior in DMSO (Fig. 3). Despite the presence of rigid anthracene moiety in its backbone, it exhibited a gradual increase in inherent viscosity with the decrease in polymer concentration [49] and also obeyed the empirical Fuoss equation [50], which is usually applied to random coiled polyelectrolytes: $\eta_{\text{inh}} = A / (1 + BC^{0.5}) \Rightarrow (\eta_{\text{inh}})^{-1} = 1/A + B/AC^{0.5}$, where A and B are constants; η_{inh} and C are usual notations. Its intrinsic viscosity, $[\eta]$, value from the intercept of Fuoss plot was found to be 4.62 dL/g in DMSO at 35 °C. Its relatively high $[\eta]$ value

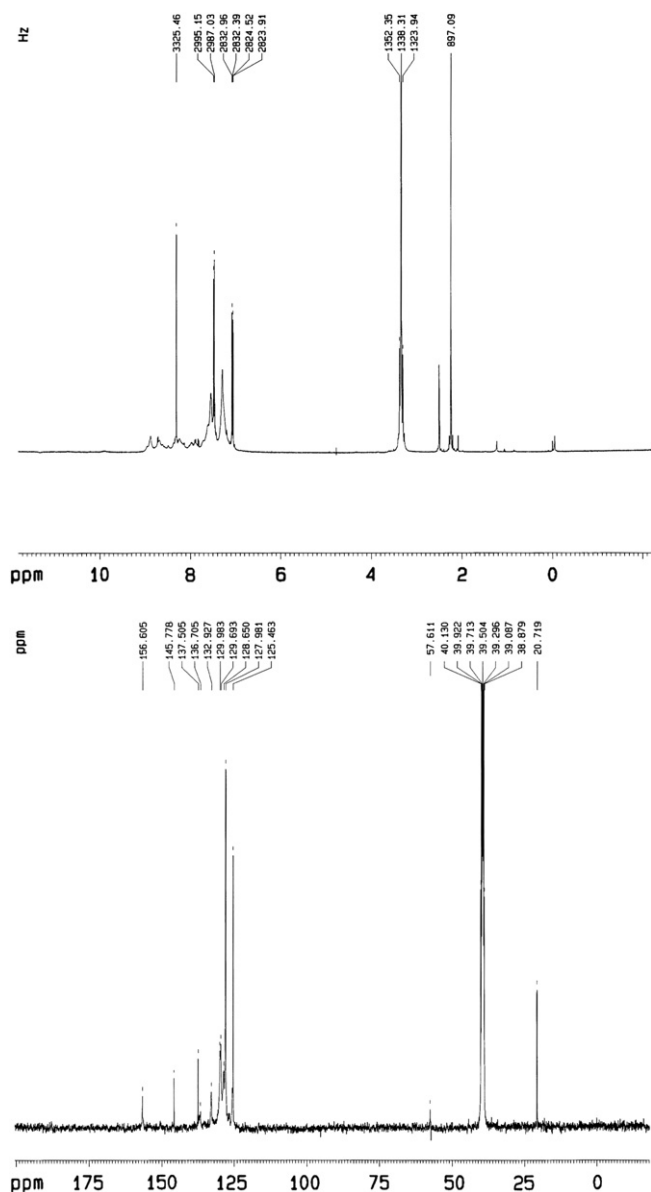


Fig. 1. ^1H (top) and ^{13}C (bottom) NMR spectra of polymer **I-1** in d_6 -DMSO taken at room temperature.

and the absence of end groups in its ^1H NMR spectrum were indicative of its reasonably high molecular weight. Like polymer **I-1**, polymer **I-2** also had identical molecular weights, since it was prepared by metathesis reaction from polymer **I-1**. Furthermore, both of them had finger-nail-creasable film, forming properties from a number of common organic solvents that included methanol, acetonitrile, and DMSO.

3.3. Lyotropic liquid-crystalline properties

Many π -conjugated anthracene polymers are usually prepared through the soluble precursor methods, since they are insoluble in various organic solvents [8,13–15]. In contrast, polymer **I-1**, which was an ionic, conjugated anthracene polymer, containing tosylate as counterion not only had a relatively high solubility in DMSO but also exceeded the critical

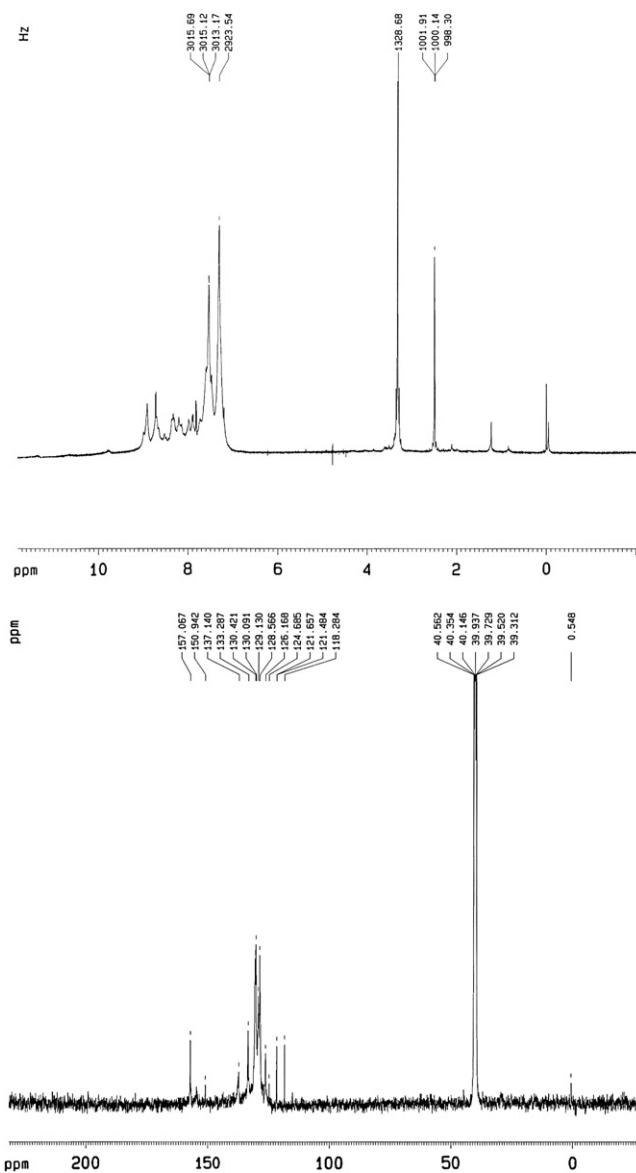


Fig. 2. ^1H (top) and ^{13}C (bottom) NMR spectra of polymer **I-2** in d_6 -DMSO taken at room temperature.

concentration (C^*) for the formation of an LC phase in this solvent at room temperature. Its C^* for the formation of a biphasic solution and the concentration of fully-grown LC phase (Fig. 4) were 20 and 40 wt%, respectively, at room temperature. Its biphasic solution exhibited both an isotropic and anisotropic phases, which were not separable from each other. In contrast, this polymer also exhibited biphasic solutions at 10 and 20 wt% in methanol and acetonitrile, respectively, from which both isotropic and anisotropic phases could be separated easily. Polymer **I-2** containing triflimide as a counterion also had high solubility in DMSO like polymer **I-1**, but the development of LC texture was not quite evident due to the high viscosity of these polymer solutions. The slow evaporation of a 10 wt% of this polymer in DMSO solution exhibited clearly an anisotropic phase suggestive of the formation of lyotropic phase of this polymer in this solvent.

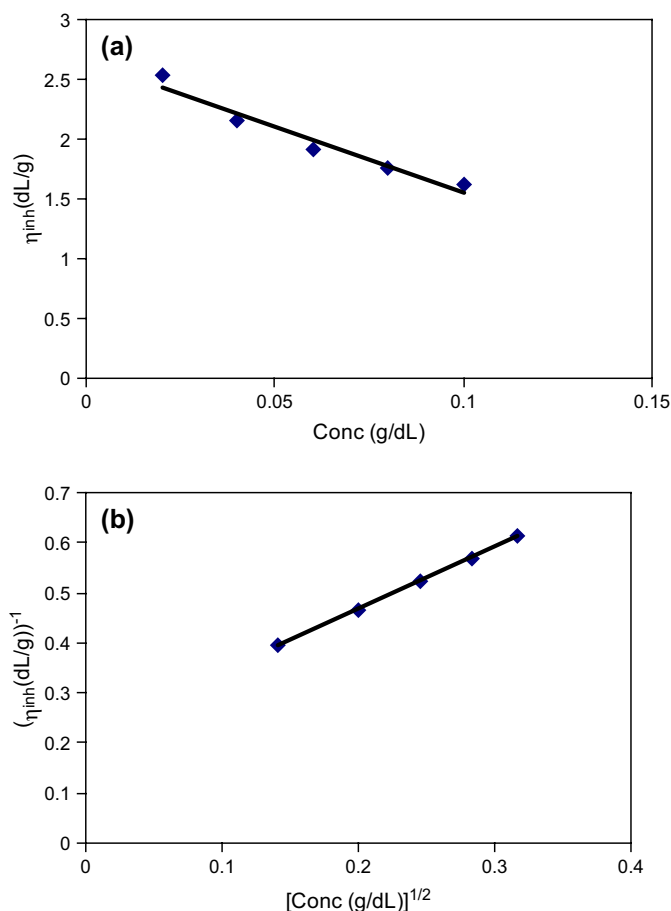


Fig. 3. Polyelectrolyte behavior of: (a) polymer **I-1** in DMSO at 35 °C and (b) its Fuoss plot.

Furthermore, it formed a fully-grown lyotropic phase at 40 wt% in acetonitrile (Fig. 4), but it, unlike polymer **I-1**, had very low solubility in methanol that precluded the formation of LC phase in this solvent. The textures observed with the PLM studies for biphasic and lyotropic solutions in various solvents for these polymers, like other poly(pyridinium salt)s [23–25] exhibited different types of polygonal arrays—often referred to as mosaic textures (Fig. 4a)—and individual rounded droplets consisting of characteristic Maltese crosses, all of which were indicative of their lamellar phase [23–25,51]. Interestingly enough, the texture of biphasic and lyotropic solutions of these polymers was preserved on the slow evaporation of either DMSO or methanol or acetonitrile. However, the exact nature of biphasic and homogeneous birefringent textures observed for these polymers at various concentrations in various solvents needs to be identified by X-ray diffraction technique, and the results from this study will be reported elsewhere.

3.4. UV–vis and photoluminescence properties

Because both the polymers **I-1** and **I-2** contained 4,4'-(1,4-phenylene)bis(2,6-diphenylpyridinium) ion and anthracene moieties in the main chain that act as chromophores, they were examined for their optical properties both in solution

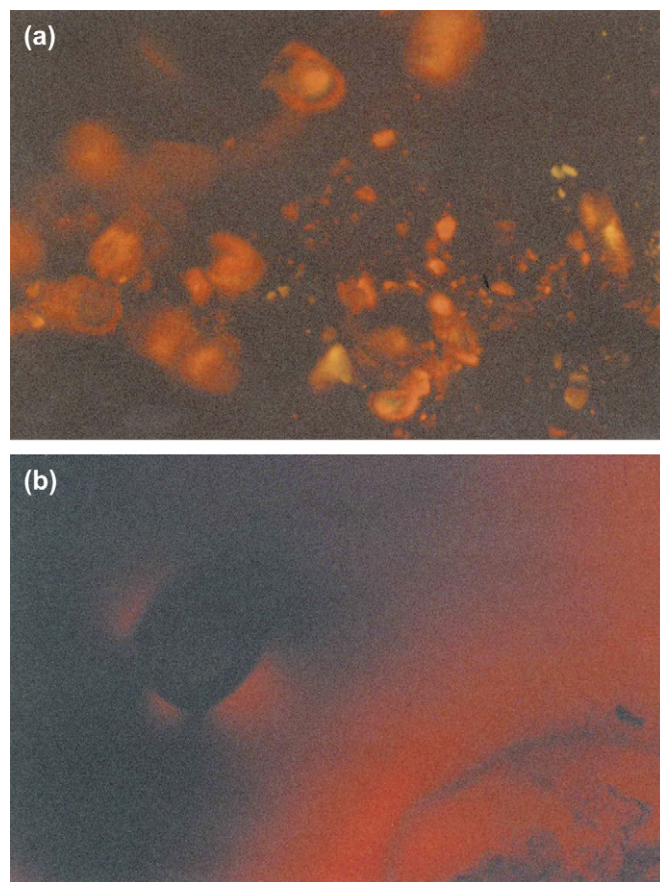


Fig. 4. Photomicrographs of: (a) polymer **I-1** at 40 wt% in DMSO and (b) polymer **I-2** at 40 wt% in CH₃CN under crossed polarizers exhibiting lyotropic LC phases (magnification 400×).

and in the solid state. Both of them had identical absorption spectra in DMSO ($\epsilon = 48.9$) and displayed absorption maxima at 265 and 348 nm in their UV–vis spectra in this solvent. Polymer **I-1** exhibited absorption maxima at 260 and 345 nm in methanol ($\epsilon = 32.6$) in its UV–vis spectra. Similarly, polymer **I-2** also exhibited absorption maxima at 263 and 344 nm in acetonitrile ($\epsilon = 36.0$). All of these absorption maxima were indicative of closely spaced π – π^* transitions common to aromatic rings. A model compound 1,2,4,6-tetraphenylpyridinium perchlorate exhibits an absorption spectrum with a $\lambda_{max} = 312$ 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 [52]. Thus, it was reasonable to state that the absorption bands of polymers **I-1** and **I-2** arose from the combination of electronic transitions as those in closely related pyridinium and anthracene moieties. The optical band gaps of polymer **I-1** (E_g 's) as determined from the onset of wavelength in the UV–vis spectra in methanol and DMSO were 3.17 and 3.19 eV; those of polymer **I-2** in acetonitrile and DMSO were 3.24 and 3.20 eV, respectively. These band gaps were higher than those of other conjugated light-emitting polymers including poly(*p*-phenylenevinylene)s [3–6,53–55], but comparable with those of other related poly(pyridinium salt)s [56].

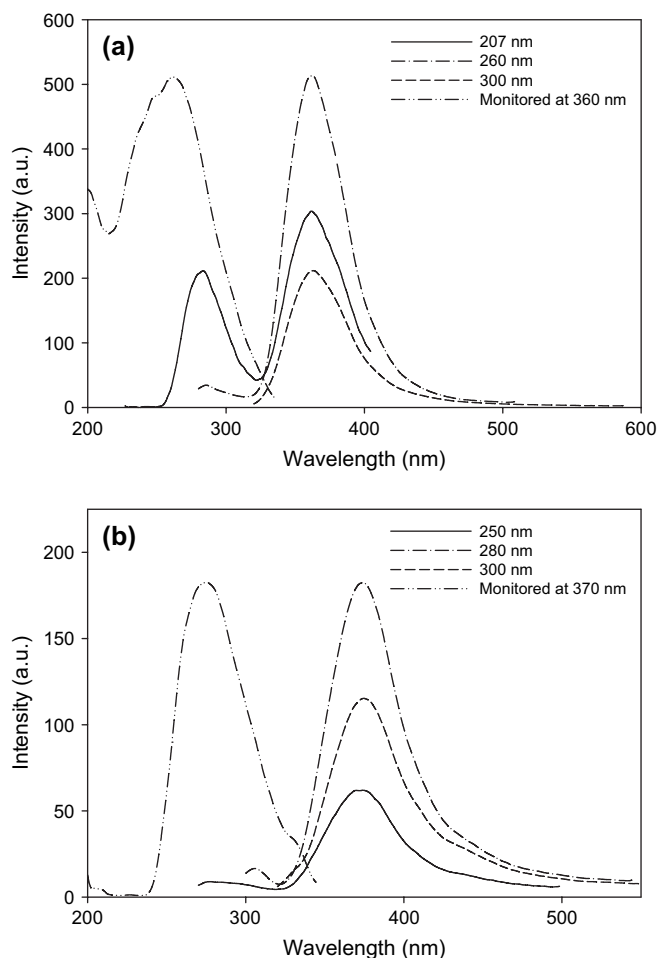


Fig. 5. Emission spectra of polymer **I-1** at various excitation wavelengths: (a) in CH_3OH and (b) in DMSO.

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 methanol and DMSO are shown in Fig. 5. In methanol, it showed an λ_{em} at 361 nm when excited at 260 and 300 nm. In another excitation wavelength of 207 nm it exhibited λ_{em} 's of 285 and 361 nm. Its λ_{ex} was located at 262 nm when monitored at 360 nm in methanol. In DMSO, it showed essentially a single λ_{em} at 370 nm when excited at 250, 280 and 300 nm. Its excitation peak remained essentially identical to that in methanol. 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 at several excitation wavelengths [57]. The emission spectra of polymer **I-2** in both acetonitrile and DMSO are shown in Fig. 6. In acetonitrile, it exhibited two distinct λ_{em} 's of 289 and 362 nm at various excitation wavelengths suggestive of the fact that multiple chromophores were present in this solvent. In DMSO, polymer **I-2** showed a single λ_{em} at 374 nm when excited at 250, 280, and 300 nm. Its λ_{ex} peak maximum was located at 275 nm when monitored at 375 nm like polymer **I-1**. The sharpness of the emission peaks also

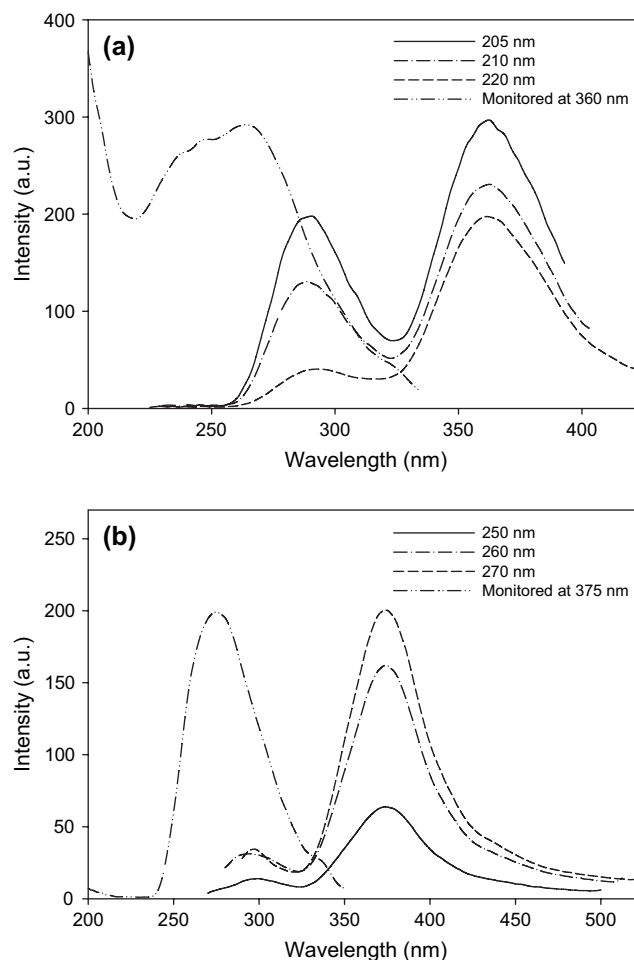


Fig. 6. Emission spectra of polymer **I-2** at various excitation wavelengths: (a) in CH_3CN and (b) in DMSO.

indicated that this polymer also had a well-defined structure, like polymer **I-1**, in this solvent [57]. These results suggested that the light emission from polymer **I-2** occurred from the identical chromophore to that of polymer **I-1** in DMSO, and was independent of the nature of counterions. Therefore, it was found that both the polymers **I-1** and **I-2** emitted light of wavelengths lower than 400 nm in various polar organic solvents, which suggested that they were UV light-emitting polymers.

The films of polymers **I-1** and **I-2** were prepared from their respective solutions (methanol or acetonitrile) casting onto quartz plates. The solid-state emission spectra of polymers **I-1** and **I-2** cast from two different solvents are shown in Fig. 7. In thin film when cast from methanol solution, polymer **I-1** showed a major λ_{em} at 390 nm and a minor λ_{em} at 280 nm when excited at 230 and 240 nm (Fig. 7a). On going from solution to the thin film, there was a slight bathochromic shift of ca. 29 nm in its λ_{em} value, when compared with that of solution spectrum. The minor peak exhibited a slight hypsochromic shift of ca. 5 nm. These features strongly suggest that there existed less ordered structures in the solid state of this polymer. The full width at half-maximum (fwhm) values of emission peaks in thin films of this polymer **I-1** were

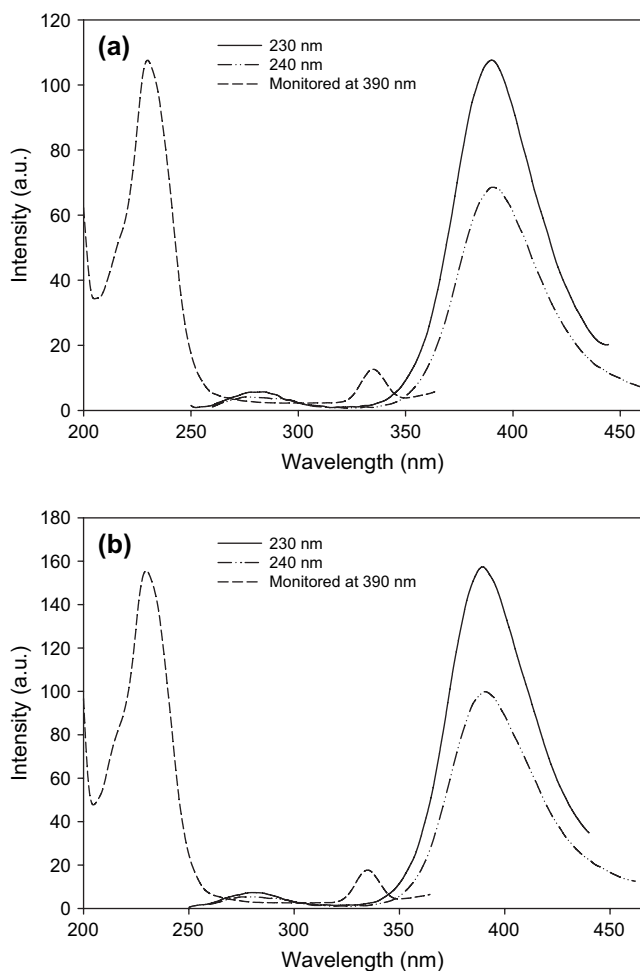


Fig. 7. Emission spectra of polymers **I-1** and **I-2** in thin films at various excitation wavelengths: (a) cast from CH_3OH solution and (b) cast from CH_3CN solution, respectively.

relatively comparable when compared with those in solution spectra. In thin film when cast from acetonitrile solution, polymer **I-2** showed a major λ_{em} at 390 nm and a minor λ_{em} at 280 nm when excited at 230 and 240 nm (Fig. 7b). On going from solution to the thin film, there was a slight bathochromic shift of 29 nm in its λ_{em} value for major peak, when compared with that of solution spectrum, like polymer **I-1**. However, the minor peak exhibited a hypsochromic shift of ca. 9 nm when compared to that in solution spectra. These features strongly suggest that there also existed less ordered structures in the solid state of this polymer. The fwhm values of emission peaks in thin films of this polymer **I-2** were also relatively comparable when compared with those in solution spectra. Note here that both intra- and intermolecular π – π 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 [58,59]. These π – π interactions of chromophores of conjugated polymers were essentially minimum in these poly(pyridinium salt)s containing anthracene moieties. Their light emission also occurred in the solid state in the UV region of the light. In recent years there is

considerable development of organic light-emitting devices (OLEDs) that have extended the emission wavelengths over the whole visible range and enabled to the realization of full-color displays [60]. Extending the emission of OLEDs into even shorter ultraviolet wavelengths may find many uses in biological/fluorescence sensors and in full-color displays by generating blue-to-red emission through pumping in luminescent materials. To date, there are few conjugated polymers that emit UV light, since it is difficult to realize UV emission with π -conjugated polymers [61,62]. In this regard, polymers **I-1** and **I-2** are the recent addition of ionic, conjugated polymers that emit UV light that make them novel and attractive for potential technological applications.

4. Conclusions

They are the first examples of poly(pyridinium salt)s with anthracene moieties in the main chain containing tosylate and triflimide counterions that exhibited lyotropic LC in polar organic solvents and UV light-emitting properties both in solutions as well as in the solid state. The combination of lyotropic 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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