Polymer Communication

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

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This article is dedicated to Professor Robert W. Lenz with best wishes on the occasion of his 75th birthday.

Abstract

Two poly(pyridinium salt)s containing a bulky organic counterion such as 2-naphthalenesulfonate were synthesized by the ring-transmutation polymerization reaction of bis(pyrylium 2-naphthalenesulfonate) with the corresponding aromatic diamines on heating in dimethyl sulfoxide (DMSO) at 145–150 °C for 24 h, and characterized for their lyotropic liquid crystalline as well as fluorescence properties in both polar protic and aprotic solvents such as methanol and DMSO. Their polyelectrolyte behavior in DMSO was also determined by solution viscosity measurements. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(pyridinium salt); Lyotropic; Photoluminescence

1. Introduction

Recently, nitrogen-containing polymers have received an unabated attention in the design and synthesis of electroluminescent polymers. They typically consist of π-electron-deficient heterocycles containing imine nitrogen in the aromatic moieties. They usually include poly(2,5-pyridylene)—an analogue of poly(p-phenylene), poly(2,5-pyridylenevinylene)—an analogue of poly(p-phenylenevinylene), poly(oxadiazole), poly(triazole), poly(triazine), poly(quinoline), poly(quinoxaline), poly(4-vinylpyridine), poly(aniline), and poly(pyrrole), among others. Unlike other π-conjugated polymers, all of these polymers contain nitrogen heteroatoms either in the main chains or in the side chains that provide facile quaternization reaction as well as protonation of the nitrogen sites. Thus, their emission spectra can be tuned at will by adding a charged species to a nitrogen site by manipulating their electronic structures [1–7]. Besides their electroluminescent properties, conducting and liquid crystalline (LC) properties (lyotropic and thermotropic) of suitably designed polymer structures make them attractive materials in many technological applications [8–11]. Additionally, there are two other main-chain poly(pyridinium) salts that are also relevant to this class of

polymers. One typically consists of 4,4′-bipyridinium ions along the backbone of the polymer chains that are known as viologen polymers, which exhibit a number of interesting properties including electrical conductivity, electrochromism, photochromism, thermochromism, and both thermotropic and lyotropic LC properties. The other consists of phenylated aromatic pyridinium salts along the backbone of the polymer chains. All aromatic systems are desirable because of their high thermal and chemical stability. These polymers, 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 [12,13]. Harris et al. reported the synthesis of this class of polymers containing tetrafluoroborate, an inorganic counterion, by the ring-transmutation polymerization reaction and the characterization of their physical properties. Although their glass transition temperature, T_g, values cannot be determined by the differential scanning calorimetry (DSC) measurements, they exhibit distinct melting endotherms with a minimum above 380 °C. Thermogravimetric analyses (TGA) indicate that they start to decompose at about 360 °C prior to their melting transition temperature, T_m, values. 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

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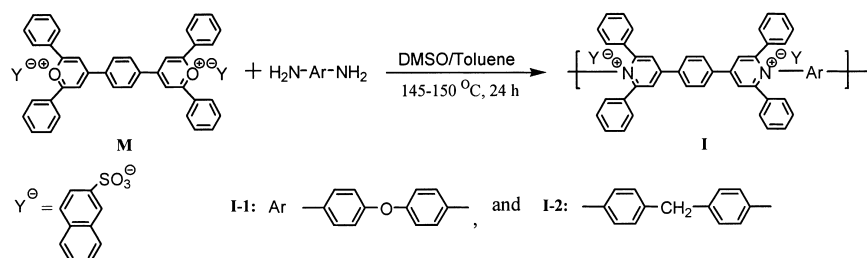
Scheme 1. Ring-transmutation polymerization reaction of bis(pyrylium salt) with aromatic diamines.

these solvents is insufficient to form lyotropic solutions at room temperature [13]. Recently, Huang et al. reported the results of another series of poly(pyridinium salt)s with a triflate counterion. These polymers were significantly more thermally and thermooxidatively stable than analogous poly(pyridinium) salts with a tetrafluoroborate counterion. They were also soluble in polar aprotic organic solvents including dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMAc) from which fingernail-creasable films were easily cast [14].

In this communication, we describe the synthesis of two new aromatic ionic polymers—poly(pyridinium salt)s—containing a bulky organic counterion such as 2-naphthalenesulfonate ion by the ring-transmutation polymerization reaction of bis(pyrylium salt) with aromatic diamines and the characterization of their lyotropic properties in polar protic and aprotic 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. In contrast to an inorganic counterion such as tetrafluoroborate, the presence of a bulky 2-naphthalenesulfonate counterion in each of these ionic polymers increases the solubility both in methanol and DMSO by significantly reducing the strong ionic interactions between positive and negative charges. Additionally, this bulky organic counterion provides a mechanism to achieve its solubility to such an extent that each of them exceeds its critical concentration, C^*, to form lyotropic LC phase in these organic solvents. To our knowledge, they are the novel examples of poly(pyridinium salt)s with 2-naphthalenesulfonate counterion that exhibit lyotropic properties in both polar protic and aprotic solvents. Furthermore, they exhibit photoluminescence (PL) in both polar protic and aprotic solvents.

2. Experimental section

2.1. Monomer synthesis

The 4,4′-(1,4-phenylene)bis[2,6-diphenylpyrylium 2-naphthalenesulfonate], **M**, was synthesized by the modification of a procedure by which the corresponding bis(tetrafluoroborate) salt had been prepared [13]. In this procedure, terephthalaldehyde was condensed with more than four

equivalents of acetophenone to afford the desired tetra-ketone, which was subsequently cyclodehydrated to **M** by treatment with triphenylmethyl-2-naphthalenesulfonate. The hydride acceptor was generated in situ from triphenyl-methanol and 2-naphthalenesulfonic acid. The procedure for the preparation of tetraketone was as follows. A mixture of terephthalaldehyde (10.0 g, 0.075 mol) and acetophenone (54.3 g, 0.45 mol) was stirred in 250 ml of 95% ethanol and heated to 65 °C. After the starting compounds dissolved in aqueous ethanol, a solution of KOH (10.5 g, 0.19 mol) in 10 ml of water was added dropwise over 30 min with vigorous stirring. A yellow precipitate formed immediately. The heterogeneous reaction mixture was then heated at reflux until it turned pink, occurring over a period of 4–5 h. During this time, the *p*-bischalcone redissolved and reacted with two additional equivalents of acetophenone to form the desired tetraketone, which precipitated. The reaction mixture was filtered hot, and the tan solid was collected by filtration to afford 41.0 g of the crude product. It was recrystallized from toluene to afford 35.0 g (yield 81%) of off-white crystals: it showed a melting endotherm at T_{max} at 206 °C (mp 205–206 °C [13]) as determined by DSC at a heating rate of 10 °C/min. The conversion of tetraketone to **M** was carried out in accordance with the following procedure. Triphenylmethanol (8.1 g, 0.031 mol) and 2-naphthalenesulfonic acid monohydrate (7.0 g, 0.031 mol) were added to 100 ml of $(CH_3CO)_2O$, followed with stirring at room temperature for 3 h. Then, the solid tetraketone (7.2 g, 0.012 mol) was added to the reaction mixture, and the mixture was heated to 100 °C for 1 h. The heterogeneous reaction mixture became clear. Upon cooling, yellow crystals appeared and were collected by filtration, washed carefully with $(CH_3CO)_2O$ and ethanol, respectively, and dried in air to afford the crude **M**. It was then recrystallized from acetic acid and dried in vacuum to afford 6.5 g (6.81 mmol) of orange-colored **M** (yield 57%). It showed a glass transition temperature, T_g, at 96 °C and several endothermic transitions at 158 (T_m), 203, 300, and 312 °C (T_i) as determined by DSC at a heating rate of 10 °C/min. Its purity was also checked by ^1H NMR spectroscopy, and elemental analysis. δ_H (DMSO-d_6, 400 MHz, ppm): 9.32 (4H, s, aromatic *meta* to O$^+$), 8.61 (4H, m, 1,4-phenylene), 7.48–8.12 (34H, m, phenyl and 2-naphthyl). Anal. calcd for $C_{60}H_{42}O_8S_2$: C, 75.45; H, 4.43; S, 6.71. Found: C, 74.21; H, 4.37; S, 6.68. The 4,4′-oxydianiline (99 + %, sublimed,
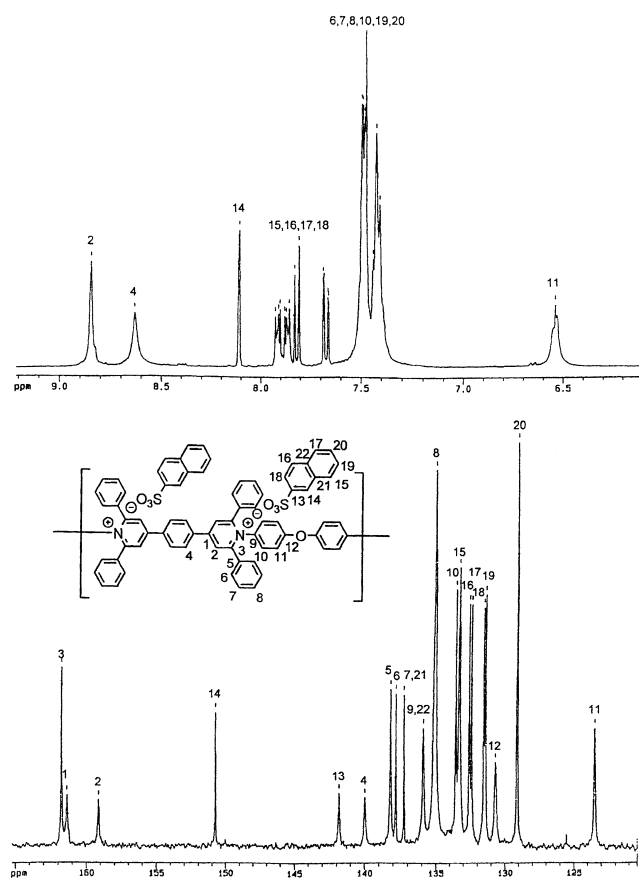
Fig. 1. ^{1}H and ^{13}C NMR spectra of polymer **I-1** in DMSO-d_6 taken at room temperature.

zone-refined) was received from Aldrich Chemical Co. and used without further purification. The 4,4'-methylenedianiline (purity 97%) was also received from Aldrich Chemical Co. and further purified by recrystallization from EtOH/H$_2$O.

2.2. Polymer synthesis

The bis(pyrylium salt) **M** was polymerized with either 4,4'-oxydianiline or 4,4'-methylenedianiline by the ring-transmutation polymerization reaction [13] that was carried out on heating in DMSO at 145–150 °C for 24 h, shown in Scheme 1. The water generated during the polymerization was distilled from the polymerization medium as a toluene/water azeotrope. The poly(pyridinium salt)s were essentially isolated in quantitative yield by precipitation with the addition of ethyl acetate. Each of them was further purified by redissolving in DMSO and by subsequent re-precipitation with the addition of water. Each of these polymers precipitated out in powder form, unlike the analogous poly-(pyridinium salt) with triflate counterion that formed fibrous structure [14]. However, they had finger-nail-creasable film forming properties from both DMSO and methanol. The ^{1}H and ^{13}C NMR spectra of polymer **I-1** are shown in Fig. 1 with its relative assignments of

various chemical shifts. The corresponding spectral data of polymer **I-2** are as follows: δ_H (DMSO-d_6, 400 MHz, ppm): 8.83 (4H, s, aromatic *meta* to N$^+$), 8.62 (4H, s, 1,4-phenylene), 7.40–8.11 (38H, m, phenyl, 2-naphthyl, and *meta* to –CH$_2$–), 6.54 (4H, m, *ortho* to –CH$_2$–), 2.50 (2H, s, CH$_2$); δ_c (DMSO-d_6, 100 MHz, ppm): 161.76, 161.37, 159.17, 150.74, 141.84, 139.97, 138.16, 137.83, 137.26, 135.90, 135.04, 133.56, 133.31, 132.60, 132.45, 131.56, 131.44, 130.71, 129.13, 123.51, 44.65.

Additionally, their ^{13}C NMR spectra contained only aromatic carbon signals between 123 and 162 ppm. The carbonyl resonance at 186.8 ppm, which is attributable to a vinylogous amide [15], was not detected suggesting that the ring-transmutation polymerization reaction proceeded to completion for the synthesis of these two polymers. The proton signals of vinylogous amide and amino end-groups were also not detected in their ^{1}H NMR spectra. The association of 2-naphthalenesulfonate counterions around poly-(pyridinium salt)s because of π–π stacking interactions of naphthalene rings were not detected, since their proton signals did not exhibit an up-field shift of ring protons due to an increased magnetic shielding accompanied by a remarkable signal broadening. It is important to note here that the association of 2-naphthalenesulfonate counterions around poly(allylammonium) cations because of π–π stacking interactions of naphthalene rings is detected by ^{1}H NMR in D$_2$O by the observation of both an up-field shift and a remarkable line broadening of naphthalene ring protons [16]. Anal. calcd for C$_{72}$H$_{50}$N$_2$O$_7$S$_2$ (**I-1**): C, 77.26; H, 4.50; N, 2.50; S, 5.73. Found: C, 75.57; H, 4.74; N, 2.50; S, 5.58. Anal. calcd for C$_{73}$H$_{52}$N$_2$O$_6$S$_2$ (**I-2**): C, 78.47; H, 4.69; N, 2.51; S, 5.74. Found: C, 75.30; H, 5.24; N, 2.51; S, 5.67.

2.3. Polymer characterization

The ^{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 DMSO-d_6 using TMS as an internal standard. The inherent viscosity, IV, values of the polymers were measured in methanol and DMSO, whenever possible, at various concentrations with a Cannon-Ubbelohde-type viscometer at 35 °C. The polarizing light microscope (PLM) study was performed with a PLM (Nikon, Model Labophot 2) equipped with crossed polarizers and a hot stage. Solutions of these ionic polymers for the study of lyotropic properties were prepared by mixing known amounts of polymer and a specific solvent (methanol or DMSO) and then shaking for a period of 7 d for equilibration. Their absorption spectra in spectrograde DMSO and methanol were recorded with a Varian Cary 3 Bio UV–Vis Spectrophotometer at ambient temperature. Their PL spectra in solutions were recorded with a SLM 4800 spectrofluorometer at ambient temperature.
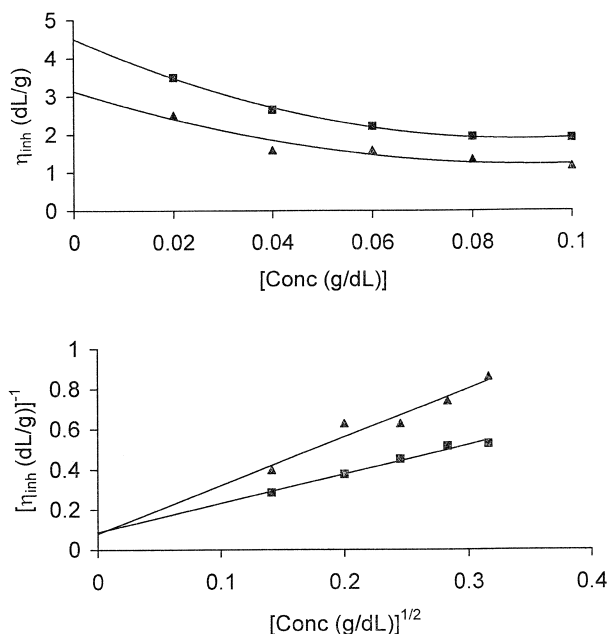
Fig. 2. (a) Polyelectrolyte behavior of polymers **I-1** (■) and **I-2** (▲) in DMSO at 35 °C; (b) Fuoss plots of polymers **I-1** (■) and **I-2** (▲).
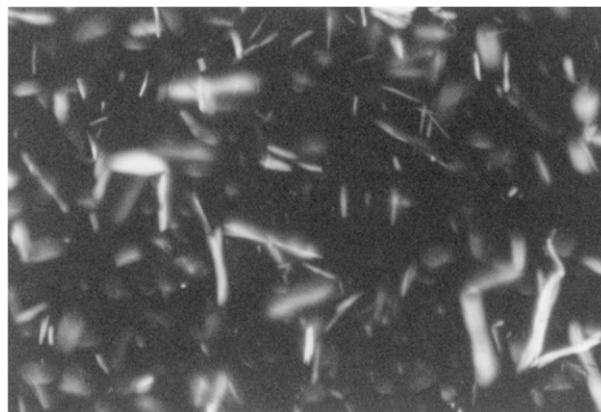

Fig. 3. Photomicrograph of polymer **I-2** at 29 wt% in DMSO taken at room temperature under cross-polarizers exhibiting biphasic solution (magnification 400 ×).

3. Results and discussion

Because of the presence of 4,4′-(1,4-phenylene)bis[2,6-diphenylpyridinium 2-naphthalenesulfonate] ions along the backbone of the polymer chain, each of these polymers, **I-1** and **I-2**, showed a polyelectrolyte behavior in DMSO for a concentration range 0.02–0.10 g/dl, that is, the IV of polymer solution increased with the decrease in polymer concentration (Fig. 2(a)). As expected, these two polymers obeyed the empirical Fuoss equation [17], which is usually applied to flexible polyelectrolytes, in DMSO: $\eta_{inh} = A/(1 + BC^{0.5}) \Rightarrow (\eta_{inh})^{-1} = 1/A + B/AC^{0.5}$, where A and B are constants; η_{inh} and C are usual notations. Despite the presence of flexible ether and methylene linkages in the backbone of these polymers, their intrinsic viscosity values obtained from the intercepts of Fuoss plots (Fig. 2(b)) were 11.4 and 12.3 dl/g in DMSO at 35 °C, respectively, indicative of their relatively high molecular weights. Their fingernail-creasable film forming properties from DMSO and methanol were also indicative of their high molecular weights. However, when compared with the IV (8.3 dl/g) of analogous poly(pyridinium salt) with triflate counterion in DMSO (0.12 g/dl) at 30 °C [14], the IV of polymer **I-1** was found to be 1.7 dl/g under similar conditions, which was rather low.

The analogous poly(pyridinium salt)s of **I-1** with either a tetrafluoroborate or a triflate ion do not exhibit lyotropic LC properties in polar aprotic solvents including DMF, DMAc, and DMSO because of their insufficient solubility in these solvents [13,14]. In contrast, polymer **I-1** formed biphasic solutions in methanol over a range of concentrations of 5–10 wt%, which transformed on standing into two distinct

phases. These two phases were easily separable and identified as an anisotropic (lyotropic) and isotropic phase by PLM studies. In contrast, it formed an isotropic solution as high as 20 wt% in DMSO at room temperature. On further increase in its concentration in this solvent, it exhibited biphasic solutions over a broad range of concentrations of 29–50 wt%. In each of these biphasic solutions an LC phase coexisted with an isotropic phase, which could not be separable. As expected, with the increase in its wt% in this solvent, the development of LC phase increased with the expense of an isotropic phase up to 50 wt%. At 60 wt% in DMSO it exhibited a fully grown lyotropic phase. Similar to polymer **I-1**, polymer **I-2** also formed biphasic solutions in methanol for a range of concentrations of 5–20 wt%, which on standing transformed into anisotropic and isotropic phases that could be easily separable. It also formed an isotropic solution as high as 20 wt% in DMSO. Its biphasic solutions, from which anisotropic and isotropic phases could not be separable, persisted over a broad range of concentrations of 29–50 wt%. At the highest concentration, it exhibited a fully developed lyotropic solution at its 60 wt% in this solvent. The textures observed with the PLM studies for each of these biphasic and lyotropic solutions in methanol and DMSO for these two poly(pyridinium salt)s showed small and large bâtonnets, different types of polygonal arrays—often referred to as mosaic textures (Fig. 3)—and individual rounded droplets consisting of characteristic Maltese crosses, all of which were indicative of their lamellar phase [18]. Interestingly enough, the texture of either the biphasic solution or lyotropic solution of these polymers was preserved on the slow evaporation of either DMSO or methanol.

Despite the presence of three chromophores (namely, substituted bispyridinium, 4,4′-oxydianiline, and 2-naphthalenesulfonate) in polymer **I-1**, it had a single absorption band at $\lambda_{max} = 337$ nm in methanol in the UV–Vis spectrum, indicative of closely spaced $\pi-\pi^*$ transitions common to aromatic rings. A model compound, 1,2,4,6-tetraphenylpyridinium perchlorate, exhibits essentially an identical
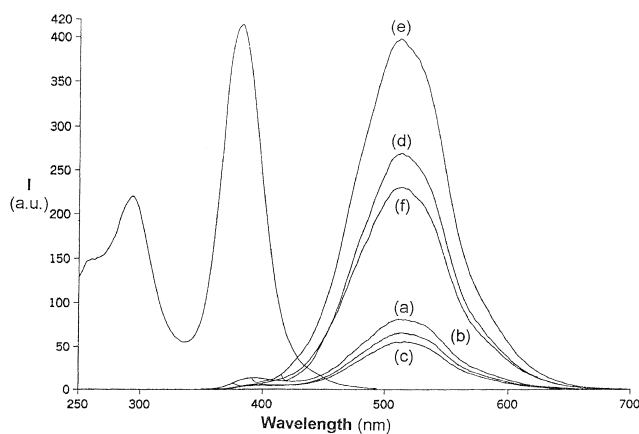
Fig. 4. Excitation spectrum monitored at 512 nm and emission spectra of polymer **I-1** at excitation wavelengths (a) 320, (b) 337, (c) 345, (d) 366, (e) 376, and (f) 400 nm in methanol.
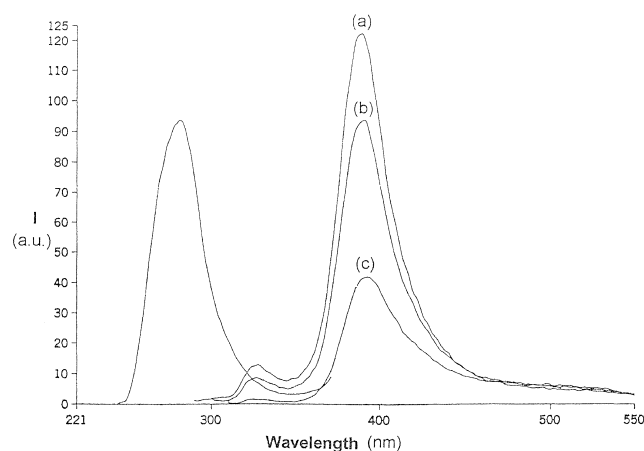

Fig. 5. Excitation spectrum monitored at 400 nm and emission spectra of polymer **I-2** at excitation wavelengths (a) 280, (b) 290, and (c) 300 nm in DMSO.

absorption spectrum with a $\lambda_{max} = 312$ nm in ethanol. The absorption band of o-substituted pyridinium salt consists of two electronic transitions. They are intramolecular charge transfer complexes of the 2,6- and the 4-substituent with the positively charged nitrogen center [19]. Thus, it was reasonable to state that the absorption band of polymer **I-1** arose from the same electronic transitions as those in closely related pyridinium salts. Additionally, it had a substantial contribution from the electronic transitions of 2-naphthalenesulfonate counterion. It is important to note here that the absorption band of sodium-2-naphthalenesulfonate in water has a $\lambda_{max} = 280$ nm along with a number of fine vibrational structures [16]. Its both excitation and emission spectra in methanol solution are shown in Fig. 4. Each of its emission spectra excited at various wavelengths showed at $\lambda_{em} = 515$ nm, but the intensity of emission spectrum depended on the excitation wavelength used. It exhibited an excitation spectrum that consisted of two bands ($\lambda_{ex} = 294$ and 382 nm) when excited at 512 nm. In DMSO, it had essentially an identical absorption band ($\lambda_{max} = 342$ nm) to that in methanol, suggesting that its absorption maximum was less sensitive to the polarity of these two solvents. This result also implied that the interactions of each of these two solvents and repeating units of this polymer were of minor importance in the ground state. However, it showed an excitation spectrum in DMSO that contained a single peak, unlike in methanol, at $\lambda_{ex} = 282$ nm when monitored at 395 nm. Each of its emission spectra in this solvent contained a principal peak ($\lambda_{em} = 395$ nm) and a shoulder peak ($\lambda_{em} = 515$ nm) when excited at 280, 290, and 300 nm. The intensity of emission spectrum was the highest at excitation wavelength of 280 nm and the lowest at excitation wavelength of 300 nm. Therefore, it was found that the λ_{em} of polymer **I-1** in this solvent when compared with that of methanol showed a hypsochromic effect, that is, blue shift by 120 nm.

Similar to polymer **I-1**, polymer **I-2** had essentially identical absorption ($\lambda_{max} = 337$ nm), emission ($\lambda_{em} = 492$ nm

at excitation wavelengths 320, 337, 360, and 375 nm; $\lambda_{em} = 496$ nm at excitation wavelength 390 nm), and excitation spectra ($\lambda_{ex} = 244$, 331, and 361 nm when monitored at 493 nm) with the minor exceptions to those of polymer **I-1** in methanol. These exceptions include the blue shift of λ_{em} by 23 nm and the appearance of an additional excitation band. It also showed an excitation spectrum that consisted of λ_{ex} values at 237, 277, and 377 nm when monitored at 754 nm. It had essentially an identical absorption spectrum in DMSO ($\lambda_{max} = 340$ nm) to that of polymer **I-1**. Its excitation spectrum and emission spectra in this solvent are shown in Fig. 5. Similar to polymer **I-1**, its excitation spectrum consisted of one peak at $\lambda_{ex} = 282$ nm when monitored at 400 nm and each of its emission spectra consisted of a single peak at $\lambda_{em} = 390$ nm. The intensity of emission spectrum was dependent on the excitation wavelength used. Therefore, it was observed that the λ_{em} of polymer **I-2** in this solvent, like polymer **I-1**, when compared with that of methanol showed a blue shift by 102 nm.

The optical band gaps of polymers **I-1** and **I-2** as determined from the onset of wavelength in the UV–Vis absorption spectra in both methanol and DMSO were 3.25, 3.19, 3.27, and 3.22 eV, respectively. These band gaps were higher than those of other conjugated light emitting polymers including poly(p-phenylenevinylene)s [1,2,20], but comparable with those of other related poly(pyridinium salt)s [21]. It was also determined that the UV–Vis spectra of these two polymers in both methanol and DMSO were essentially independent of the structures of the aromatic diamines used. Additionally, both of them exhibited a large Stokes shift in methanol (178 and 150 nm) and a relatively small Stokes shift (53 and 50 nm) in DMSO, respectively. The large difference in Stokes shift for each of them was related to the very different geometry of the ground and excited states of its repeating unit in these two solvents. The solutions of two rigid-rod polyamides

containing *p*-terphenyl or *p*-quinquephenyl moieties in the backbone as well as 2-naphthyl pendent groups in CCl$_3$COOH have neither fluorescence nor lyotropic properties [22], but polymers **I-1** and **I-2** containing 2-naphthalenesulfonate as a counterion exhibited violet-blue fluorescence in DMSO having λ_{em} values at 395 and 390 nm, respectively, as well as lyotropic LC property.

4. Conclusions

The combination of a lyotropic LC property, the ease of film formation, and violet-blue/violet-green PL makes these polymers an interesting class of ionic polymers. They might offer an opportunity for the exploitation of optoelectronic applications including polymeric light emitting, and photovoltaic devices as well as light emitting electrochemical cells. Furthermore, they are ideal cationic polyelectrolytes for the build-up of multilayer assemblies with controlled morphologies at a molecular level by the sequential deposition technique with other negatively charged polyelectrolytes for optoelectronic applications.

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