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

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Recently, nitrogen-containing polymers have received unabated attention in the design and synthesis of electroluminescent polymers.[1−10] They typically consist of π-electron-deficient heterocycles containing imine nitrogen in the aromatic moieties. They usually include poly(2,5-pyridylene),[11] an analogue of poly(*p*-phenylene),[12−15] poly(2,5-pyridylenevinylene),[10] an analogue of poly(*p*-phenylenevinylene),[12−15] poly(oxadiazole),[16] poly(triazole),[17] poly(triazine),[18] poly(quinoline),[19,20] poly(quinoxaline),[21] poly(4-vinylpyridine),[22] poly(aniline),[23] and poly(pyrrole),[23] among others. Unlike other π-conjugated polymers,[12−15] all of these polymers contain nitrogen heteroatoms 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.[1−10] Besides their electroluminescent properties,[1−10] conducting[24] and liquid-crystalline (LC)[25−27] 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,[28] electrochromism,[29] photochromism,[30] thermochromism,[31] and LC properties.[32,33] The other consists of 4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium) ions along the backbone of the polymer chains. All-aromatic systems are desirable because of their high thermal and chemical stability. 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.[34] Harris et al. reported the synthesis of this class of polymers containing $^{-}BF_4$, 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 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 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 these solvents is insufficient to form lyotropic solutions.[34] Recently, Huang et al. reported the results of another series of poly(pyridinium salt)s with triflate as a counterion. These polymers were significantly more thermally and thermooxidatively stable than analogous poly(pyridinium) salts with $^{-}BF_4$ counterion. They were also soluble in polar organic solvents including dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and dimethylacetamide (DMAc) from which fingernail creasable films were easily cast.[35]

In this communication, we describe the synthesis of a new series of aromatic ionic polymers—poly(pyridinium salt)s—containing a bulky organic counterion such as tosylate ion 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 Scheme 1. In contrast to the $^{-}BF_4$ counterion, the presence of a bulky tosylate counterion in each of them increases its solubility in both methanol and DMSO by significantly reducing the strong ionic interactions between positive and negative charges. Additionally, this organic counterion provides a mechanism to achieve its solubility to such an extent that each of them exceeds its critical concentration, C^*, to form a lyotropic LC phase in these organic solvents. They are the first examples of poly(pyridinium salt)s with tosylate as a counterion that exhibit lyotropic properties in both protic and aprotic polar solvents. They also exhibit photoluminescence both in solution and in the solid state.

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-1S** (prepared in a small scale, 3 g), **I-1L** (prepared in a large scale, 20 g), and **I-2** (also prepared in a small scale, 3 g), showed a polyelectrolyte behavior in DMSO. The polymers **I-1S** and **I-1L** also exhibited the polyelectrolyte behavior in methanol. As expected, these two polymers obeyed the empirical Fuoss equation,[36] which is usually applied to random coiled polyelectrolytes, in both DMSO and methanol: $\eta_{inh} = A/(1+ BC^{0.5}) \Rightarrow (\eta_{inh})^{-1} = 1/A + B/AC^{0.5}$, where A and B are constants; η_{inh} and C are usual notations. Their intrinsic viscosity values obtained from the intercepts of Fuoss plots were 11 and 253 dL/g in DMSO, respectively, at 35 °C, indicative of their relatively high molecular weights. In contrast, the polymer **I-2** did not obey the Fuoss plot, suggesting its rigid-rod-like character as expected. The size exclusion chromatographs of polymer **I-1L**, obtained by using a Viscotek model triple detector array, were indicative of the fact that signal-to-noise for each of these chromatographs was excellent for all three detectors. Its M_n, M_w and M_z values were 41 000, 56 000, and 76 000, respectively, and its polydispersity index (M_w/M_n) was 1.4. Two other solution parameters, measured in DMSO at 70 °C, were also calculated: these are radius of gyration, R_g, and hydrodyanamic radius, R_h. They were 9.11 and 7.00 nm, respectively. Furthermore, its calculated Mark−

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

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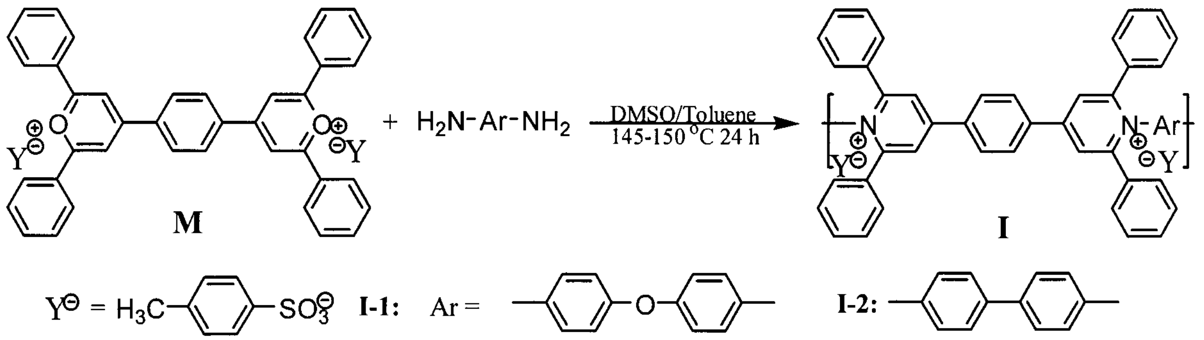
Scheme 1



Houwink α and K values were 1.16 and 1.3 × 10^{-6} dL/g, respectively, in DMSO and 70 °C.

Poly(pyridinium salt)s with either $^{-}BF_4$ or triflate ion do not exhibit lyotropic properties in polar aprotic solvents including DMF, DMAc, and DMSO (vide supra) because of their insufficient solubility in these solvents.[34,35] In contrast, the polymers containing tosylate counterion (**I-1S**, **I-1L**, and **I-2**) not only had the solubility in DMSO but also exhibited lyotropic properties in DMSO above their C^* values. They also exhibited lyotropic properties in a polar protic solvent such as methanol. Similar to nonionic lyotropic LC polymers, both **I-1S** and **I-1L** usually formed an isotropic solution at 20 wt % in methanol. At an intermediate concentration 30 wt % each of them exhibited a biphasic solution in which an LC phase coexisted with an isotropic solution. At relatively high concentration 40 wt % each of them formed a fully grown lyotropic phase. Similarly, they also formed biphasic and lyotropic solutions in DMSO at 20 and 30 wt %, respectively. Despite the large difference in their molecular weights, it was found that their C^* values for the formation of a lyotropic phase were essentially identical in these solvents. Furthermore, the C^* values were lower in DMSO than those in methanol. As expected, the C^* value of polymer **I-2** for the formation of a lyotropic phase in DMSO was lower (10 wt %) than those of polymers **I-1S** and **I-1L** (20 wt %) because of its more rodlike structure. It formed a fully grown lyotropic phase at 19 wt % in DMSO. Additionally, unlike its biphasic solution in DMSO, it formed a biphasic solution in methanol at a very low concentration of 5 wt %, which transformed on standing into two distinct phases. These two phases were easily separable and identified as an anisotropic and an isotropic phase by PLM studies. Their LC textures for each of these biphasic and lyotropic solutions in these solvents showed small and large bâtonnets, different types of polygonal arrays—often referred to as mosaic textures (Figure 1)—and individual rounded droplets consisting of characteristic Maltese crosses, all of which were indicative of their lamellar phase.[37]

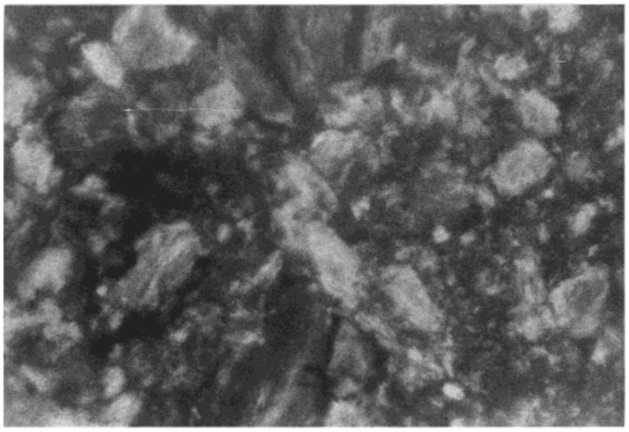


Figure 1. Photomicrograph of polymer **I-2** at 31 wt % in DMSO taken at room temperature under crossed polars exhibiting lyotropic solution (magnification 400×).

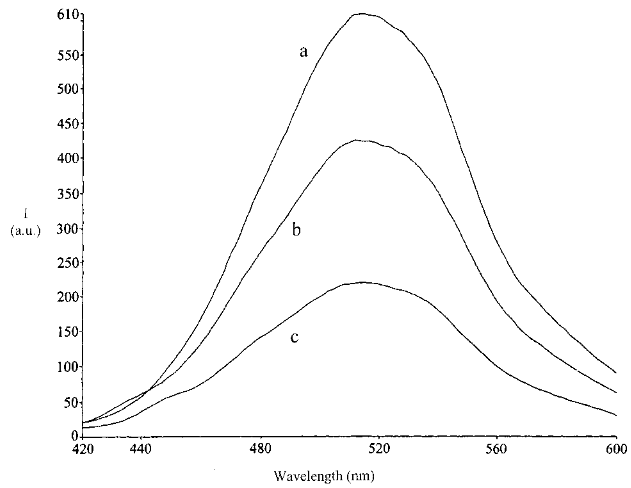


Figure 2. Emission spectra of polymer **I-1L** in methanol solution at excitation wavelengths (a) 345, (b) 384, and (c) 394 nm.

Polymer **I-1L** in methanol had an absorption band at λ_{max} = 335 nm in the UV–vis spectrum. Each of its emission spectra, recorded from the methanol solution at various excitation wavelengths of light (345, 384, and 394 nm), showed a very broad band centered at about 500 ± 20 nm as shown in Figure 2. In contrast, each of the emission spectra of its thin film cast from methanol at excitation wavelengths 345 and 360 nm showed a number of vibrational fine structures (Figure 3). These emission spectra were centered at about 460 ± 20 nm and were blue-shifted compared to those in the solution spectra. Polymer **I-2** in DMSO had an absorption band at λ_{max} = 347 nm in the UV–vis spectrum. Its excitation spectrum (λ_{ex} = 386 nm with a shoulder at 368 nm) resembled the absorption spectrum with the exception that it was slightly red-shifted with respect to its absorption spectrum. As usual, its emission spectra (λ_{em} = 518 nm with a shoulder at 543 nm) were independent of its excitation wavelengths (347, 368, and 386 nm). An analogous poly(pyridinium salt)-containing $^{-}BF_4$ counterion in DMF at ambient temperature has an absorption, excitation, and emission maxima at 348 (350), 348 (365), and 485 nm as reported by Makowski and Mattice.[38] The emission spectrum of polymer **I-2**

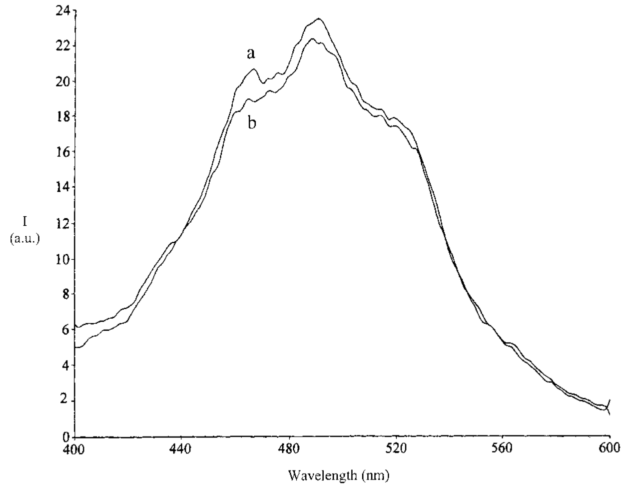


Figure 3. Emission spectra of polymer **I-1L** in thin film cast from methanol solution at excitation wavelengths (a) 345 and (b) 360 nm.

in DMSO was red-shifted with respect to that of poly(pyridinium salt) containing $^{-}BF_4$ counterion in DMF.

In conclusion, the combination of lyotropic LC property, the ease of film formation, and photoluminescence makes these polymers interesting for optoelectronic applications such as polymeric light-emitting devices. They are also ideal cationic polyelectrolytes for the buildup of multilayer assemblies with controlled morphologies at a molecular level by the sequential deposition technique with other negatively charged polyelectrolytes.

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Supporting Information Available: Monomer synthesis (**M**), polymer synthesis, and polymer characterization; ^{1}H and ^{13}C NMR spectra of polymer **I-1S** (Figure S1), polyelectrolyte behavior of polymers **I-1S**, **I-1L**, and **I-2** in CH_3OH and DMSO (Figure S2), SEC traces of polymer **I-1L** in DMSO at 70 °C (Figure S3), and photomicrograph of polymer **I-1S** in methanol (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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