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Lyotropic Liquid Crystalline Main-Chain Viologen Polymers: Homopolymer of 4,4′-Bipyridyl with the Ditosylate of *trans*-1,4-Cyclohexanedimethanol and Its Copolymers with the Ditosylate of 1,8-Octanediol

Pradip K. Bhowmik,*,† Abul H. Molla,† Haesook Han,† Mahinda E. Gangoda,‡ and Rathindra N. Bose‡

Department of Chemistry, University of Detroit Mercy, 4001 West McNichols Road, P.O. Box 19900, Detroit, Michigan 48219-0900, and Department of Chemistry, Kent State University, P.O. Box 5190, Kent, Ohio 44242-0001.

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ABSTRACT: A series of viologen polymers based on 4,4′-bipyridyl and the ditosylates of *trans*-1,4-cyclohexanedimethanol and 1,8-octanediol was prepared by the quaternization reaction in acetonitrile. Their polyelectrolyte behavior in a common organic solvent was studied by viscosity measurements, and their chemical structures were determined by FTIR and 1D and 2D NMR spectroscopies. They were characterized for their lyotropic properties in a number of polar organic solvents by polarizing light microscopy and differential scanning calorimetry and for their photochromic properties by UV−vis spectroscopy. As expected, their inherent viscosity in methanol decreased dramatically with the increase in concentration in the absence of an added electrolyte. Although each of these polymers contained the ionic group along the backbone of the polymer chain, there was an array of weak ion-pair dipoles between the tosylate ion and the 4,4′-bipyridinium ion in each of them, which was indicated by the appearance of symmetric stretching band of S═O at a lower frequency (1034 cm^{-1}) when compared with that of $-SO_3Na$ (1064 cm^{-1}) in its IR spectrum. The aromatic protons of 4,4′-bipyridinium ion in each of these polymers exhibited three pairs of signals as opposed to a pair of doublets that generally occurs in small molecules containing this ion. These three pairs of signals were related to the structure and dynamics of these ionic polymers in a polar solvent such as methanol, which were studied by DEPT, $^1H-^1H$ COSY, and NOESY spectroscopies. Each of them showed a lyotropic lamellar phase in methanol, ethanol, ethylene glycol, diethylene glycol, glycerine, and benzyl alcohol. Their critical concentrations (C^* values) were as low as 5 wt % and as high as 20−40 wt %, and their concentrations for the development of fully grown lyotropic phase were as low as 10−20 wt % and as high as 40−50 wt % in various alcohols depending on the polarity of the solvents, the hydrophilicity and hydrophobicity of the solvents, and the microstructures of these polymers. Additionally, their lyotropic solutions in either glycerine or benzyl alcohol, on irradiation with UV light, produced a deep blue color in the presence of air, but in absence of both a photosensitizer and a sacrificial donor. This deep blue solution had two absorption bands at 390 and 608 nm, which are the characteristic absorption bands of the viologen cation radical. The generation of this blue color occurred due to the photoreduction of the 4,4′-bipyridinium moiety via the electron transfer from the tosylate counterion.

Introduction

The 1,1′-dialkyl-4,4′-bipyridinium salts are commonly called viologens. Viologen polymers are an important class of materials, which exhibit a wide range of properties including electrical conductivity, photochromism, electrochromism, thermochromism, and photomechanical behavior.[1−6] They are also known as ionene polymers because of the presence of 4,4′-bipyridinium ions in the polymer backbone. The liquid crystallinities, that is, both the thermotropic and lyotropic properties of main-chain ionic polymers, have received considerable attention in the field of LCPs. Blumstein and co-workers described the thermotropic properties of a series of ionene polymers prepared from the quaternization reaction of *trans*-1,2-bis(4-pyridyl)ethylene with $X-(CH_2)_n-X$ (where, $n = 4-10, 12, 16$; X = mesylate and tosylate). They are crystalline and exhibit two endotherms in a differential scanning calorimetry (DSC) thermogram. The first endotherm is related to the hydration of ionic sites and the second to the crystal-to-LC transition (T_m). The two polymers with $n = 7$ and 9 have T_m values lower than those of the other polymers in this series. They, on heating above their respective T_m values, display the simultaneous flow and birefringence indicative of a S_A phase, as determined with the polarizing light microscope (PLM) and small-angle X-ray scattering (SAXS) studies. However, the mobility of the LC phase is reduced, ceasing above 150 °C because of the cross-linking and oxidation reactions. Other polymers have T_m values close to the cross-linking temperature (>150 °C), which precludes the observation of a LC phase. Their T_m values are reported to be a function of both the number of methylene units and the size of the counterions. Furthermore, they are soluble in water and ethanol, exhibiting lyotropic LC behavior in these solvents. The critical concentration (C^*) of such a polymer with $n = 7$ and mesylate as a counterion is 70 wt % in water at room temperature, and it increases with the increase in temperature.[7−10] Jegal and Blumstein also described

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* To whom correspondence should be addressed. Present address: Materials Research Laboratory, Polaroid Corp., 750 Main St., 5C, Cambridge, MA 02139.

† University of Detroit Mercy.

‡ Kent State University.

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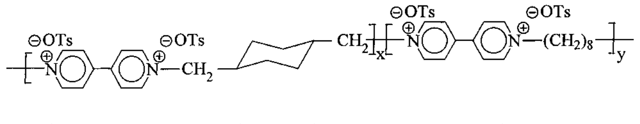
the thermotropic properties of a few other ionene polymers based on either 1,2-bis(4-pyridyl)ethane (BPE) or 1,4-diazabicyclo[2.2.2]octane (DABCO). The two polymers containing bromide as a counterion, prepared from the quaternization reaction of either BPE or DABCO with bis((7-bromoheptanoyl)oxy)-4,4′-biphenyl, have high T_m values because of strong ionic interactions and, therefore, decompose immediately on melting. In contrast, the ionic polymer containing the tosylate as a counterion, prepared from the quaternization reaction of BPE with bis(9-(tosyloxy)nonoxy)-4,4′-biphenyl, has a crystal-to-smectic transition (T_m) at 166 °C and a smectic-to-isotropic transition (T_i) at 230 °C, respectively. Additionally, it forms a lyotropic phase at its 70 wt % in ethanol at room temperature.[10−12] Harris and co-workers reported the physical properties of a series of phenyl-substituted aromatic poly(pyridinium tetrafluoroborates)—wholly aromatic ionenes, which are prepared from the polymerization reaction of 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) with various aromatic diamines in a dimethyl sulfoxide (DMSO)/toluene mixture at 145−150 °C. All of them are insoluble in water but soluble in polar, aprotic solvents and can be solution cast into tough, flexible films. Although their glass transition temperatures (T_g values) cannot be detected with the DSC measurements, they exhibit distinctive melting endotherms with a minimum above 380 °C. Thermogravimetric analyses (TGA) indicate that they start to decompose at about 360 °C prior to melting. Furthermore, the extent of their solubility is insufficient to form lyotropic solutions in polar organic solvents at room temperature.[13] We reported that the main-chain viologen polymers are an amphotropic class of polymers. They are prepared by the quaternization reaction of 4,4′-bipyridyl with α,ω-methylene ditosylates in acetonitrile. They form smectic phases above their T_m values and undergo smectic-to-isotropic transitions (T_i values). They also exhibit a lyotropic LC phase in polar organic solvents including methanol and ethylene glycol. Their C^* values are dependent both on the number of methylene units in a polymer and on the nature of polar solvents.[14−19] Recently, we also reported the results of thermotropic properties of another series of viologen polymers that are prepared by the quaternization reaction of 4,4′-bipyridyl with either the ditosylate of *trans*-1,4-cyclohexanedimethanol or the ditosylates of *trans*-1,4-cyclohexanedimethanol and 1,8-octanediol with variable compositions in acetonitrile.[20] In this article, we describe the preparation of an extended, identical series of viologen polymers and the characterization of their lyotropic properties in a number of polar organic solvents. The general structure and designations of the viologen polymers, **I,** which were prepared and characterized in this study, are shown below:



I-1 ($x = 1.0$, $y = 0.0$); **I-2** ($x = 0.8$, $y = 0.2$);
I-3 ($x = 0.6$, $y = 0.4$); **I-4** ($x = 0.5$, $y = 0.5$);
I-5 ($x = 0.4$, $y = 0.6$); **I-6** ($x = 0.2$, $y = 0.8$)

In the field of LCPs, the *trans*-1,4-cyclohexanedimethylene unit (CDM), on one hand, is used in a number of thermotropic polyesters, but not in lyotropic polyamides.[21,22] The *trans*-1,4-cyclohexane unit, on the other hand, is used extensively in both thermotropic polyesters and lyotropic polyamides.[23,24] Therefore, it was the principal objective to study the lyotropic and other properties of these viologen polymers containing the CDM units. They were characterized by a number of experimental techniques, including solution viscosity, Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), UV−vis spectroscopy, PLM, and DSC.

Experimental Section

Monomers. The 4,4′-bipyridyl was purchased from Tokyo Kasei Kogyo Co. and purified by recrystallization twice from toluene. The ditosylate of *trans*-1,4-cyclohexanedimethanol was prepared by the reaction of a mixture of *trans/cis*-diol (70/30), obtained from Fluka, with tosyl chloride in pyridine using a standard procedure.[25] It was purified by recrystallization thrice from benzene: mp 163−164 °C (lit.[26] mp 162−163 °C). Similarly, the ditosylate of 1,8-octanediol was prepared and purified also by recrystallization twice from methanol: mp 72−73 °C (lit.[27] mp 72−73 °C). The purity of these monomers was checked by ^1H and ^{13}C NMR and elemental analysis, and the melting point by DSC.

Polymer Synthesis. Equimolar amounts of 4,4′-bipyridyl and a mixture of the ditosylates of *trans*-1,4-cyclohexanedimethanol and 1,8-octanediol were reacted under stirring in dry acetonitrile at 82 °C for 120 h.[20] During the polymerization reaction, the polymer precipitated out partially. At the end of polymerization, the reaction flask was cooled to room temperature, and the copolymer was precipitated out completely with the addition of ethyl acetate. It was filtered immediately, dried in a vacuum for 24 h, and stored in a desiccator. Similarly, the homopolymer was prepared by reacting the equimolar amounts of 4,4′-bipyridyl and the ditosylate of *trans*-1,4-cyclohexanedimethanol under an essentially identical condition.

Polymer Characterization. Infrared spectra were recorded with a Nicolet FTIR analyzer using thin films of polymers either cast from solution or in KBr pellets. The ^1H and ^{13}C NMR spectra were recorded with a Brüker AM 400 spectrometer equipped with three RF channels operating at 400 and 100.6 MHz, respectively, in CD_3OD using TMS as an internal standard. For routine analysis of one pulse proton experiment, the 6.8 μs pulse was applied with a pulse repetition interval of 20 s. A typical data acquisition process includes 8−16 K data points within the frequency window of 4000 Hz. No line-broadening factor was introduced to enhance the spectral resolution. For the ^{13}C experiments, similar acquisition parameters were employed except the spectral width was much larger, 20 000 Hz and that a 15-μs pulse was applied in a 1-s time interval. The distortionless enhancement by polarization transfer (DEPT) experiments were performed following the pulse sequence of DEPT-135. The correlated spectroscopy (COSY) and nuclear Overhauser effect spectroscopy (NOESY) experiments were performed with presaturation of the solvent peak and by using time proportional phase incrementation (TPPI) technique. Typical acquisition parameters consist of 1024 data points in F_2 and 512 data points in F_1 dimensions. A sine window function was used in the F_2 dimension. The spectral dimensions and pulse length were the same as stated for 1D measurements.

Inherent viscosities, IV, of the polymers were measured in methanol at 35 °C at various concentrations in the range 0.02−0.20 dL/g with a Cannon Ubbelohde-type viscometer. The PLM study was performed on a polarizing light microscope (Leitz, Model Ortholux) equipped with crossed polarizers and a hot stage. Solutions of these polymers were prepared by mixing known amounts of polymer and a specific solvent, including methanol, ethanol, ethylene glycol, diethylene glycol, glycerine, and benzyl alcohol and then shaking for a period of 15 days to 1 month for equilibration. The endothermic transition temperature was determined with a DSC (DuPont 910) instrument under nitrogen with heating and cooling rates

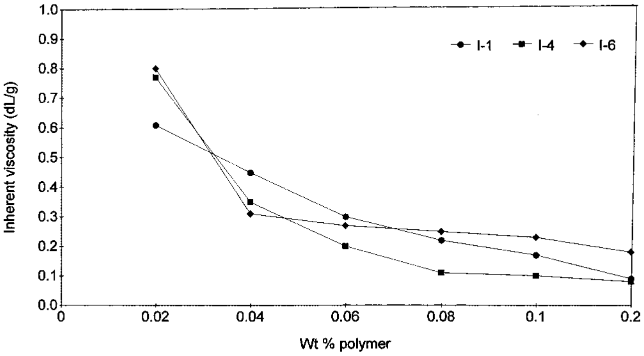


Figure 1. Inherent viscosity vs concentration of a viologen polymer measured in methanol at 35 °C, displaying a polyelectrolyte effect.

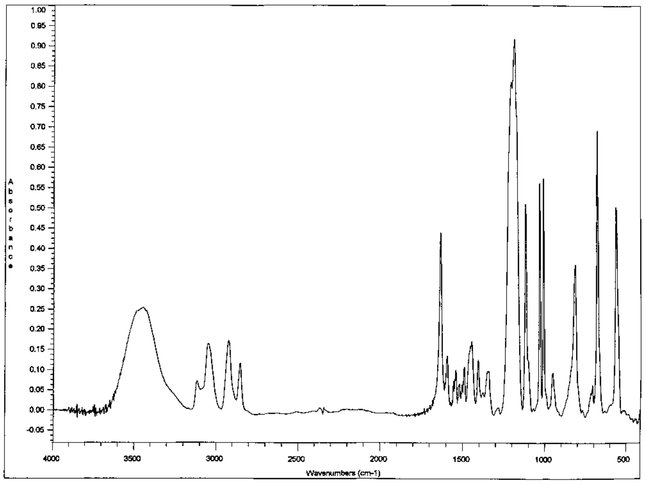


Figure 2. FTIR spectrum of polymer **I-4** in KBr pellets taken at room temperature.

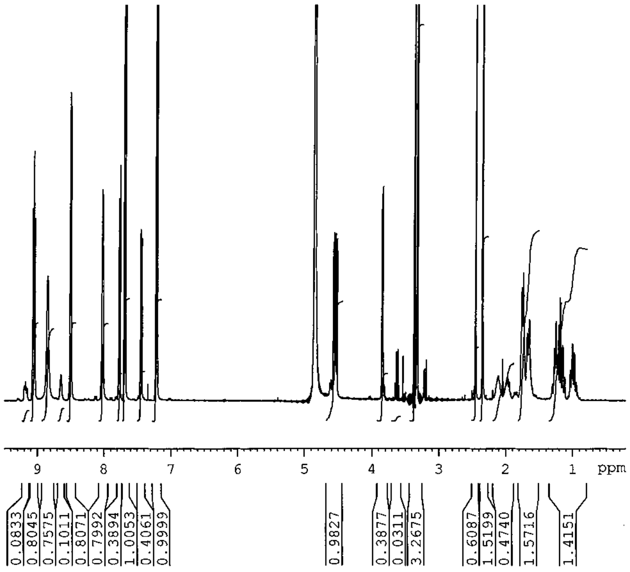


Figure 3. ^{1}H NMR spectrum of polymer **I-1** in CD_3OD.

of either 3 or 5 °C/min. The temperature axis of the DSC thermogram was calibrated prior to use with a standard of high-purity indium. A lyotropic solution in either ethylene glycol or diethylene glycol usually weighing 10−15 mg was sealed in a liquid pan holder hermetically and used for this analysis. The peak maximum of the phase transition was recorded from the DSC thermogram. The UV−vis spectra of viologen polymers in various solvents were obtained with a Hewlett-Packard 8452 diode array spectrophotometer. The spectra of their lyotropic solutions, on irradiation with UV light (Spectroline E-series UV Lamp), were also recorded with the same instrument in order to observe their photochromic (change of color with light) behavior.

Results and Discussion

Dilute Solution Properties. Because of the presence of 4,4′-bipyridinium ions along the backbone of the polymer chain, each of the viologen polymers, **I-1**−**I-6,** showed a polyelectrolyte behavior[14,28−30] in methanol, as shown in Figure 1. Their IV values in methanol in the absence of an added salt at 35 °C at a polymer concentration of 0.02 g/dL were in the range 0.61−0.80 dL/g. However, it was not possible to measure their intrinsic viscosity, [η], in the presence of an added salt such as sodium *p*-toluenesulfonate because of the limited solubility of this salt in methanol.

FTIR Spectra. Figure 2 shows the FTIR spectrum of a viologen polymer, **I-4,** recorded at room temperature in KBr pellets, which contains the representative features for all of the polymers, **I-1**−**I-6.** Their characteristic absorption bands are as follows: 3050−3120 (=C−H aromatic), 2928, 2857 (C−H aliphatic), 1495, 1410 (C−H aliphatic bending), 1210, 1190, 1175 (R−N$^+$), 1121 (S=O asymmetric stretching), 1034 (S=O symmetric stretching), 1011 (=C−H in plane bending), 956, 817 (=C−H out-of-plane bending), and 682 cm^{-1} (C=C out-of-plane bending). The asymmetric stretching of S=O occurred distinctly as a doublet. The symmetric stretching frequency of SO_3^- is very sensitive to both its counterion and physical state (solid vs liquid). Additionally, this band has been used to monitor the microstructures of poly(ethylene oxide)−$LiCF_3SO_3$ complexes and of sulfonated ionomers.[31−35] In the latter cases, for example, in both the Nafion and Dow membranes (perfluorinated ionomers), the SO_3^- symmetric stretching band is dependent on the nature of inorganic counterions and the degree of membrane hydration. This band is observed to shift to a higher frequency with the decrease in size of alkali metal counterions and the degree of hydration. This behavior is attributed to the formation of contact ion pairs, which polarize the S−O dipoles by the electrostatic field of adjacent counterions. In contrast, this band is observed to shift to a lower frequency with organic tetrabutylammonium counterion (TBA$^+$), which forms weak ion-pair dipoles relative to the strong dipole of $SO_3^-Na^+$. The band of $-SO_3H$ in the Nafion and Dow membranes appears at 1057 cm^{-1}, that of $-SO_3Na$ appears at 1064 cm^{-1}, and that of $-SO_3TBA$ appears at 1047 cm^{-1}, respectively.[35] Therefore, it was observed that this band of $^-$OTs in each of these polymers appeared at 1034 cm^{-1}, which is lower than that of $-SO_3TBA$. The low frequency of this band clearly demonstrated that there existed weak ion-pair dipoles between $^-$OTs and the 4,4′-bipyridinium ion. It is also important to note that the Raman band of S=O in solid (crystalline) $LiCF_3SO_3$ appears at 1074 cm^{-1} and that in water (free ion) appears at 1032 cm^{-1}, respectively.[36]

NMR Spectra. Figure 3 shows the ^{1}H NMR spectrum of polymer **I-1** in CD_3OD, which contained the 4,4′-bipyridinium ion with tosylate as a counterion and CDM units. Despite the simple chemical structure of the repeating units, its ^{1}H spectrum appeared to be quite complicated. The aromatic protons of the tosylate ion appeared at 7.2−7.8 ppm and those of 4,4′-bipyridinium ion at 8.0−9.2 ppm, respectively. The chemical shifts of tosylate protons remained essentially identical with

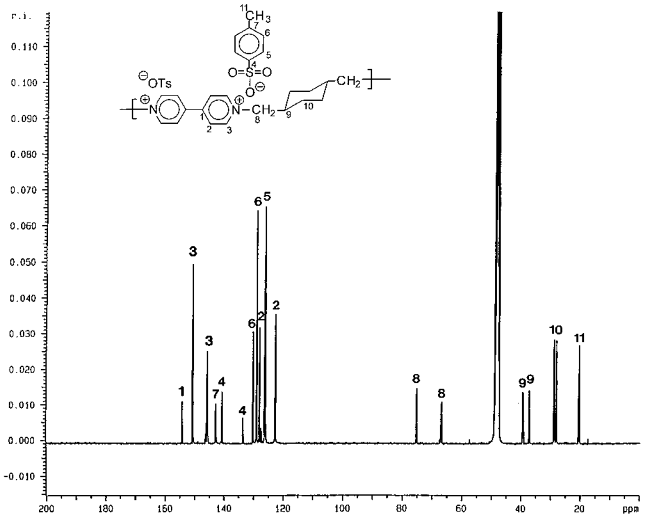


Figure 4. ^{13}C NMR spectrum of polymer **I-1** in CD$_3$OD.

those of the ditosylate of CDM, but they showed two instead of one pair of doublets. The relative intensities of these two pairs of doublets were calculated to be 0.40. The methyl protons of the tosylate ion also appeared as two singlets at 2.4 and 2.5 ppm, and their relative intensities were found to be 0.40. In contrast, the resonances of aromatic protons of the 4,4′-bipyridinium ion shifted downfield as expected compared to those of 4,4′-bipyridyl, suggesting that the quaternization reaction was complete. However, there were six sets of signals (three pairs) instead of a pair of doublets for the neutral 4,4′-bipyridyl that appears at 7.8 and 8.8 ppm, and their relative intensities were calculated to be 1:8: 8. Additionally, the exomethylene protons of the CDM unit showed two complex signals at 3.9 and 4.5−4.6 ppm. The methine and methylene protons of the CDM unit appeared strongly as overlapped resonances in the range 1.2−1.8 ppm. Its ^{13}C NMR spectrum is displayed in Figure 4 along with the relative carbon assignments. Due to the complexities in both the aromatic and aliphatic regions, including a large number of signals, the DEPT technique was used in the assignments of various carbon signals, and ^{1}H−^{1}H and ^{1}H−^{13}C COSY were used for proton assignments. The DEPT technique generally yields signals of carbons directly bonded to hydrogen. The phase of signals aids to distinguish methyl, methylene, and methine carbon atoms. Quaternary carbon does not exhibit any signal since this technique exploits selective polarization transfer from the directly bonded proton to carbon.

Figure 5 shows the ^{1}H NMR spectrum of polymer **I-4,** which contained the 4,4′-bipyridinium ion with tosylate as a counterion and equimolar amounts of CDM and octamethylene units, in CD$_3$OD. The spectrum of this copolymer exhibits qualitative features essentially identical to those of polymer **I-1.** The major difference is that the two pairs of doublets of the tosylate ion showed a tremendous disparity in intensity and their relative intensities were calculated to be 0.068 compared to 0.40 for polymer **I-1.** The two singlets of methyl protons also showed a disparity in intensity, and their relative intensities were found to be 0.068 compared to 0.40 for polymer **I-1.** Additionally, three pairs of signals of 4,4′-bipyridinium ions in this copolymer **I-4** were essentially of equal intensity. The methylene protons of the octamethylene unit next to the quaternary nitrogen appeared as multiplets between the signals of exomethylene protons of CDM unit at 4.6 ppm. Because of the complex splitting patterns of methylene protons for both units, it was difficult to quantify the copolymer composition. Its ^{13}C NMR spectrum along with the relative assignments of various carbon signals is shown in Figure 6. The DEPT technique was also used to confirm these assignments. This spectrum of polymer **I-4** also showed spectroscopic features similar to those of polymer **I-1** with a few additional features. One new feature was the appearance of methylene carbon signals next to quaternary nitrogen at 61.7 and 62.2 ppm, which were between the exomethylene signals of the CDM unit. The methyl signals of the tosylate ion appeared apparently as a single peak at 20.3 ppm, which was in contrast to the polymer **I-1** that showed distinctly two

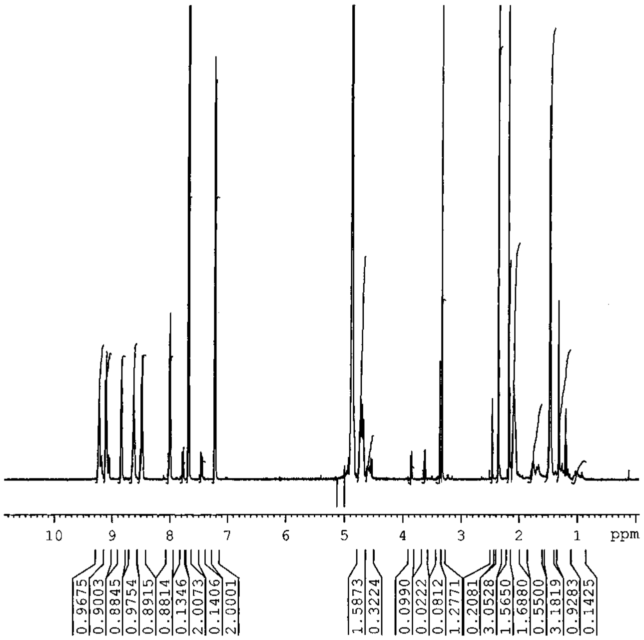


Figure 5. ^{1}H NMR spectrum of polymer **I-4** in CD$_3$OD.

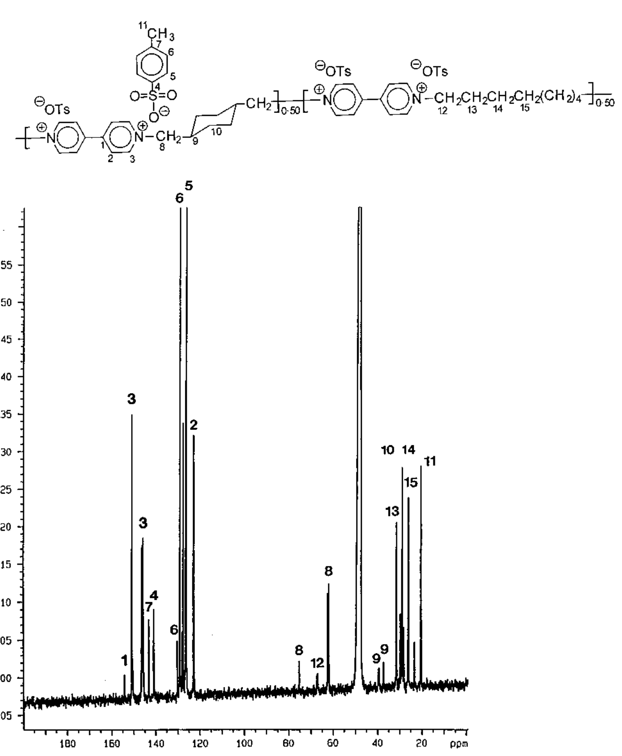


Figure 6. ^{13}C NMR spectrum of polymer **I-4** in CD$_3$OD.

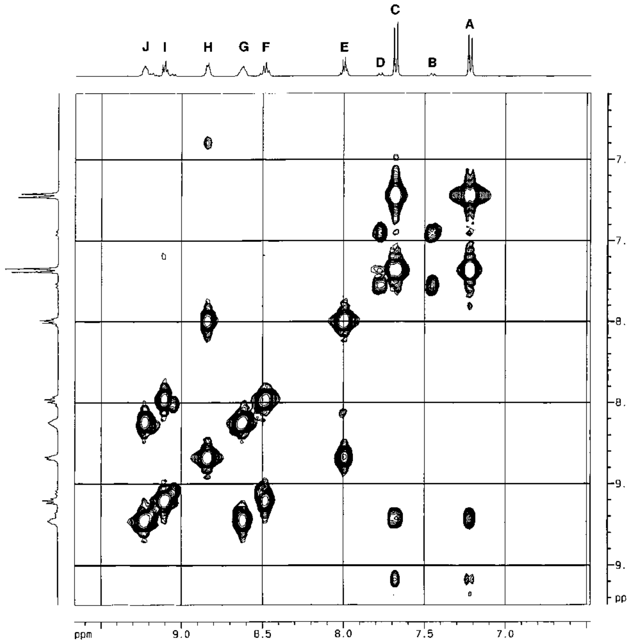


Figure 7. ^{1}H–^{1}H COSY spectrum of the aromatic region of polymer **I-4** in CD_3OD.

methyl signals at 20.3 and 20.6 ppm. Random copolymerization under the experimental condition is expected due to the structural similarity of the two ditosylates.

Figure 7 exhibits the ^{1}H–^{1}H COSY contours of the aromatic region of polymer **I-4** with projected 1D spectra in the F_1 and F_2 dimensions. The spectra reveal connectivity between each of the two sets of doublets (A + C; B + D) of the tosylate aromatic signals. In the 4,4′-bipyridinium ion there are six multiplets that can be divided in three sets through the COSY connectivity. For example, peaks E and H, F and I, and H and J display direct connectivity. On the basis of the chemical shift assignments, the first three sets of peaks (F, G, and H) can be attributed to H2 and H2′ protons and the remaining three downfield sets (H, I, and J) to H3 and H3′ protons. The existence of three separate sets of signals (E and H, F and I, and H and J) requires that the 4,4′-bipyridinium ions must exist in distinctly different electronic environments. Furthermore, since all peaks, E through J, do not appear as simple doublets, there must be a small chemical shift difference between H3 and H3′. The same is applicable to H2 and H2′ protons. Couplings between H2 and H3 as well as between H2′ and H3′ would account for four peaks observed here. Invariably, H2 and H2′ of the 4,4′-bipyridinium ion are magnetically equivalent, as are H3 and H3′. The proton spectrum of this ion in small molecules exhibits simply two doublets with a coupling constant of 7 Hz. Note that signals G and J are broader than others and lose the fine structures. The NOESY spectra exhibit all the connectivities that are observed for the COSY spectra and an additional correlation between E and F, that is, between two sets of H2 (H2′) protons.

First, we can reject the notion that the H2 and H2′ (H3 and H3′) protons of the single 4,4′-bipyridinium moiety in the copolymer exhibit markedly different chemical shifts since six multiplets are also observed for homopolymer **I-1** as well. These sets of peaks must relate to the structure and dynamics of these polymers. Two plausible explanations for these complex ^{1}H and ^{13}C spectra are provided below. First, the slow rotation of the C1–C1′ bond may lead to two (or possibly three) distinct conformations. Two pyridinium rings are positioned in either a coplanar (||) or perpendicular (⊥) fashions. These arrangements would give rise to H2(||) H2′(||), H3(||) H3′(||), H2(||) H2′(⊥), H3(||) H3′(⊥), H2(⊥) H2′(||), and H3(⊥) H3′(||) conformations. These coplanar and noncoplanar arrangements are expected to yield different chemical shifts due to the variation in the direction of ring current with respect to the magnetic field. The origin of this slow rotation of the C1–C1′ bond of the 4,4′-bipyridinium ion in these polymers is yet to be understood. However, the tosylate counterion and juxtaposed relatively rigid CDM unit collectively may impose steric hindrance that might retard the C1–C1′ bond rotation. Pure NOESY peaks can be explained on the basis of the slow exchange process (chemical exchange) between the rotamers. An alternative explanation may be more appealing, which is based on the structural motifs of linear polyelectrolyte proposed by Stevens and Kremer.[37] They, on the basis of molecular dynamics calculations, concluded that the polyelectrolyte is composed of short segments, which are stretched by Coulombic repulsions and can attain horseshoe-shaped configurations that are not rodlike. These segmental structural motifs should yield structurally and magnetically distinguishable 4,4′-bipyridinium ions resulting in distinctly different chemical shifts for H2 (H2′) and H3 (H3′) protons. The strong NOESY correlation between two sets of H2 (H2′) resonances may be due to the close proximity of these protons from 4,4′-bipyridinium ions of two distinctly different structural domains. At this point we cannot choose between the alternatives. However, the conformational studies of this type of main-chain cationic polyelectrolyte in both salt-free and salt solutions by NMR spectroscopy are in progress and will be reported elsewhere.

Lyotropic Properties. The lyotropic properties of viologen polymers, **I-1–I-6,** in various alcohols having the dielectric constants in the range of 11.9–46.5 are shown in Figure 8. Similarly to nonionic lyotropic polymers, they usually formed an isotropic solution at a low concentration. At an intermediate concentration (C^*) with a few exceptions, a biphasic solution occurred in which a LC phase coexisted with an isotropic phase. The exceptions are the polymers **I-1–I-3** in benzyl alcohol, the polymer **I-1** in ethylene glycol, and the polymers **I-1–I-6** in glycerine, each of which formed a biphasic solution as low as 1 wt %. In these cases, no attempts were made to determine their C^* values. These results suggested that their C^* values for the biphasic solutions were in the broad range of 5–40 wt % and their concentrations for the development of a fully grown lyotropic phase were also in the broad range of 10–50 wt % in these solvents. However, the relative amount of LC phase in the biphasic solution was significantly different and, consequently, the concentration for the development of a fully grown lyotropic phase was dramatically different in these various solvents. Therefore, it was found that these two solution properties were dependent on the microstructures of these polymers—that is, homopolymer vs copolymer compositions. Figure 9 shows the lyotropic properties of these polymers as a function of dielectric constants for the various alcohols. It is evident that each of the polymers, **I-1–I-3,** containing the high amounts (100, 80, and 60

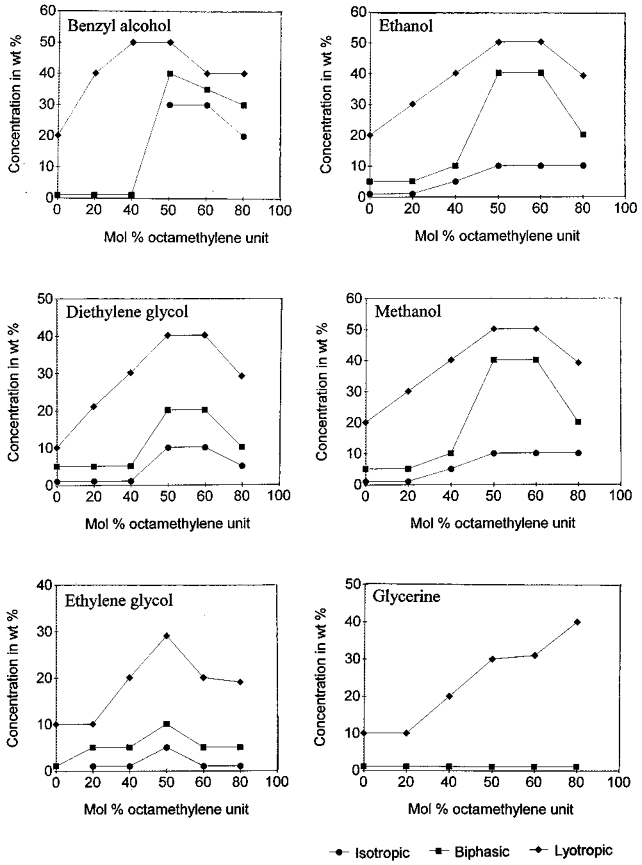


Figure 8. Lyotropic properties of viologen polymers, **I-1**–**I-6**, in various alcohols.

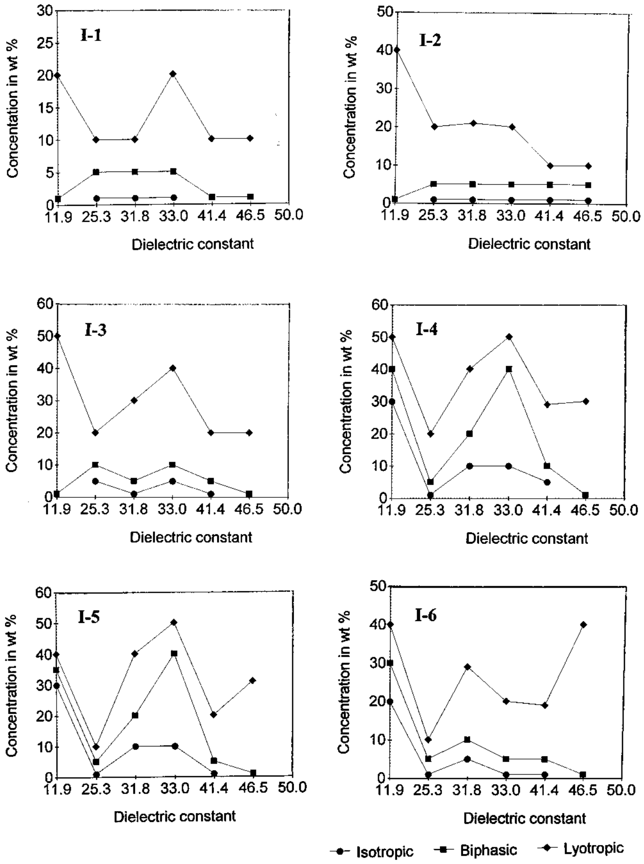


Figure 9. Lyotropic properties of viologen polymers, **I-1**–**I-6**, as a function of dielectric constants of various alcohols.

mol %, respectively) of CDM units formed a biphasic solution as low as 1 wt % in benzyl alcohol, which has the lowest dielectric constant. In contrast, each of the copolymers, **I-4**–**I-6,** containing low amounts (50, 40, and 20, respectively) of CDM units formed an isotropic solution at its high concentration (20–30 wt %) in this alcohol. Their biphasic and lyotropic solutions also occurred in the increased concentration range of 30–40 and 40–50 wt %, respectively. Their highest solubility in this alcohol among all the alcohols studied suggested that this alcohol might well offer some optimum balance of interactions with the lipophilic and lipophobic moieties of these copolymers. Additionally, all of the polymers, including the homopolymer, formed a biphasic solution as low as 1 wt % in glycerine, which has the highest dielectric constant. Again, their microstructures—homopolymer vs copolymer compositions—were the key factor for the determination of relative amounts of LC phase in their biphasic solutions and of lyotropic concentrations. On application of pressure or shear to a lyotropic phase, it caused the LC domains to deform, break, and coalesce into new ones, revealing the mobile nature of this phase. Additionally, at a higher concentration a more viscous but shearable gel resulted for each of these polymers. As representative examples, the photomicrographs of polymer **I-1** at 5 and 10 wt % in ethylene glycol when viewed with a PLM under crossed polarizers are shown in Figure 10, indicating their biphasic and lyotropic solutions, respectively. Similarly, Figure 11 shows the photomicrographs of polymer **I-1** at 20 wt % in methanol and of polymer **I-2** at 40 wt % in benzyl alcohol, indicating their lyotropic solutions.

An important feature, common to each of these polymers, was that the texture of either the biphasic or lyotropic solution was preserved on the slow evaporation of methanol. Its basic feature—that is, a threaded texture mixed with small bâtonnets or polygonal arrays (not shown)—indicated that the local orientation of LC-forming units (viologen moieties) did not change when methanol was removed by the slow evaporation process. It underwent a decrease in the density of threads with the simultaneous development of birefringence domains, which presumably occurred because of the annihilation process between disclinations of various strengths and types. Each of them gradually underwent a time-dependent transition, either from the biphasic or lyotropic solution or the methanol-evaporated film, to a crystalline phase of spherulitic structure. This observation was in good agreement with that of the previously reported other viologen polymers.[14,16] An additional feature, common to all of the biphasic solutions in either methanol or ethanol, was that they transformed on standing into two distinct (anisotropic and isotropic) phases, which were easily separable. With the gradual increase in the biphasic concentration, the amount of anisotropic phase increased at the expense of the isotropic phase, which is essentially similar to conventional lyotropic polymers in general.[38] With the slow evaporation of ethanol from all of these biphasic or lyotropic solutions, each of these polymers transformed rapidly into a crystalline phase with a spherulitic morphology, which was in contrast to that of methanol, as observed with the PLM studies. This observation was related to the varying degree of interactions of these solvents with these ionic polymers, which in turn affected the crystallization process. In contrast to their

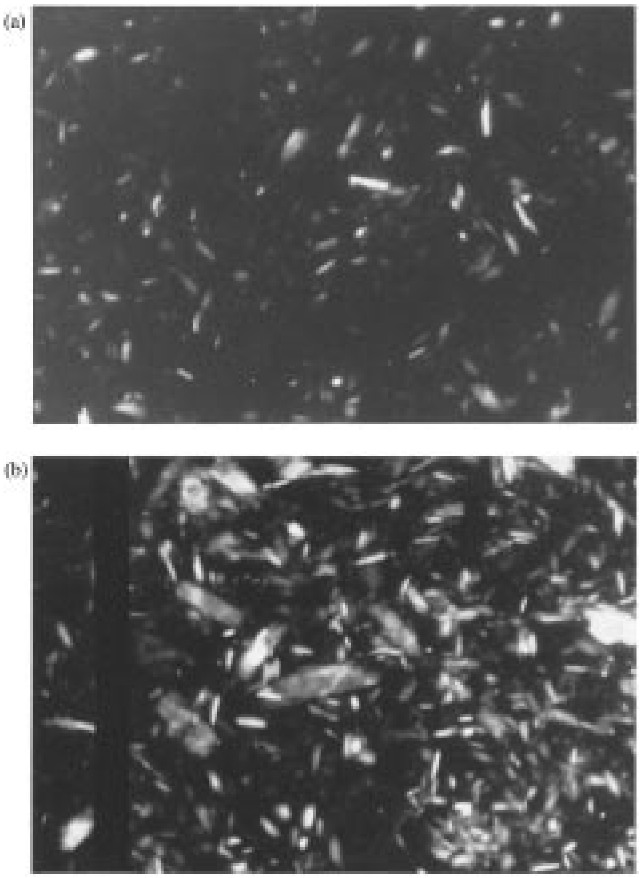


Figure 10. Photomicrographs of polymer **I-1** at 5 and 10 wt % in ethylene glycol taken at room temperature, exhibiting (a) biphasic solution and (b) lyotropic solution, respectively (magnification 400×).

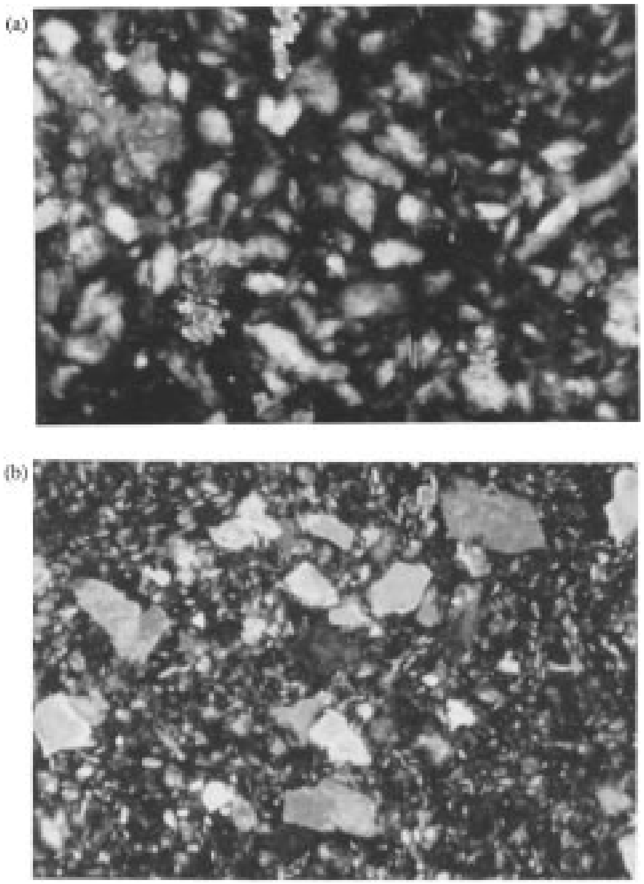


Figure 11. Photomicrographs of polymers **I-1** at 20 wt % in methanol and of polymer **I-2** at 40 wt % in benzyl alcohol taken at room temperature, exhibiting (a) and (b) lyotropic solutions (magnification 400×).

biphasic solutions in either methanol or ethanol, all of these solutions in either ethylene glycol or diethylene glycol or glycerine or benzyl alcohol on standing did not transform into two distinct (anisotropic and isotropic) phases. This observation was presumably related to either the high viscosity or the stronger interactions of the latter solvents with the polymer chain than that of the former solvents. Furthermore, the crystallization from each of these biphasic and lyotropic solutions in the latter solvents was relatively slower than that in either methanol or ethanol. In other words, the textures of their biphasic or lyotropic solutions in these various solvents could be preserved at room temperature for an appreciable period of time, typically more than 1 month. All of these results may be related to the difference in contributions of the polymer−solvent interactions (χ), especially the concentration dependence of χ in these solvents.[39] Although in the literature[40,41] there exists a considerable amount of data regarding the lyotropic phase of amphiphilic compounds in polar organic solvents, these results on lyotropic properties of these ionic polymers in these solvents offer an extension to the field of LCPs.

The formation of the lyotropic phase in a polymer is quite complex and determined by several key requirements.[24,42] The polymer usually should have a rodlike structure with an extended chain character to facilitate the alignment of the polymer chain along a particular direction. The solubility needs to be sufficiently high to exceed the *C** leading to the formation of a biphasic solution. The degree and nature of the interaction between the polymer chains themselves and that between the polymer chains and solvent molecules can provide a major influence on the phase behavior of a polymer. The solubility and chain stiffness of a polymer are themselves affected by the microstructure, molecular weight, polymer−polymer and polymer−solvent interactions, and temperature. Therefore, it was observed that the presence of ionic groups in each of these viologen polymers might increase these interactions significantly, resulting in the increased solubility and the prospect of formation of a lyotropic phase in common polar organic solvents. Additionally, copolymerization introduced the irregularities in the polymer chain, causing a decrease in crystallinity, and hence an increase in the solubility in various alcohols. Consequently, the formation of a lyotropic phase in each of these copolymers usually occurred at a much higher concentration than those of the respective homopolymers.[15] This result was in good agreement with that of the previously reported viologen copolymers.[43]

The textures of lyotropic LCPs are more or less similar to thermotropic LCPs. However, the thermotropic systems have an advantage of being one-component systems and, hence, usually less complex than the lyotropic systems that are by definition multicomponent systems.[44] A lyotropic polymer can exhibit the various textures of a nematic phase, which are usually found in the case of aromatic polyamides among others. Because of the presence of a chiral center, poly(γ-benzyl L-glutamate) shows a cholesteric texture in a number of organic solvents including benzyl alcohol.[38] The lyotropic phase may also exhibit the textures of a hexagonal phase (middle phase) and a lamellar phase (neat soap phase). These two phases are originally found in the case of amphiphilic compounds.[45] The textures observed with the PLM studies for each of the biphasic and lyotropic solutions in various alcohols having low-to-high dielectric constants for all of the viologen polymers showed small and large bâtonnets (Figure 10), and different types of polygonal arrays—often referred to as mosaic textures[46] (Figure 11), all of which were indicative of their lamellar phase.

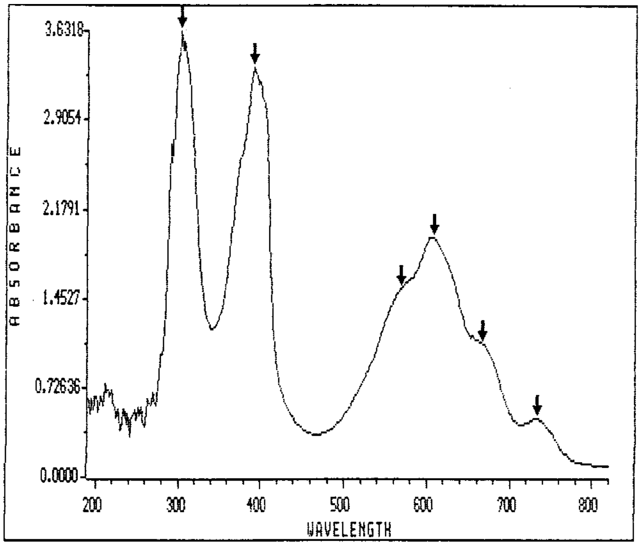


Figure 12. UV−vis spectrum of polymer **I-1** after irradiation, its lyotropic solution in glycerine with UV light indicating its deep blue solution.

At the present time, the mechanism for the formation of the lyotropic lamellar phase of these main-chain ionic polymers in various alcohols is still not well-understood. Both the polymer−polymer intermolecular interactions and the high polymer−polar solvent interactions associated with the 4,4′-bipyridinium ions seem to make an important contribution. Copolymerization seems to aid the creation of random irregularities along the polymer backbone and might also contribute to the intermolecular interactions. As far as the lyotropic lamellar phase of these polymers is concerned, their C^* values were as low as 5 wt % and as high as 20−40 wt %, and their lyotropic concentrations as low as 10−20 wt % and as high as 40−50 wt % depending on the solvents used and the microstructures of these ionic polymers. Therefore, it appears that their C^* values were rather low, despite the presence of flexible octamethylene and CDM units in their backbones. It is important to note that the C^* of (hydroxypropyl)cellulose in CH_3COOH is 30−35 wt %, that of PBLG in $CHCl_3$ is 30 wt %, and that of an alternating semiflexible copolyamide in concentrated H_2SO_4 is 25−40 wt %. Furthermore, the C^* value for each of the two well-known, wholly aromatic polyamides—poly(1,4-phenylene terephthalamide) and poly(1,4-benzamide)—is 20 wt % in 99.8% H_2SO_4. However, all of them are neutral lyotropic polymers and their C^* values are well-correlated to the persistence lengths (q values), which are equal to one-half of the Kuhn statistical segments.[24,40,47,48] The q value is a measure of how far a polymer chain persists in a given direction, it actually defines the chain rigidity. In contrast, synthetic ionic lyotropic polymers are relatively rare and are recent additions to the lyotropic LCPs.[10,18,49] Their q values are not known yet either experimentally or theoretically. Therefore, these results on lyotropic properties of viologen polymers suggest that both an extension of the current theories of polyelectrolytes to include main-chain ionic interactions and a suitable experimental technique in order to determine their q values might be worthwhile. On the contrary, many biopolymers such as TMV, DNA, cellulose microcrystals, Schizophyllan, Scleroglucan, and sickle cell hemoglobin do form lyotropic LC phases in water at various C^* values.[50] All of them are known as rodlike polyelectrolytes and have high axial ratio L/D, unlike the viologen polymers in this study. The long-range electrostatic repulsion in all of these biopolymers, as is similar in viologen polymers, influences strongly the formation of an anisotropic LC phase, as has been particularly well-documented for the case of TMV and DNA.[50] For example, Oster[51] reported that the C^* of TMV, freshly prepared by ultracentrifugation, is 2.3 wt % in water, and this nematic lyotropic solution becomes isotropic with the addition of a salt of ionic strength above 0.005 M. Wen and co-workers[52] reported the first definitive experimental observation of S_A in TMV aqueous solutions above 17.5 wt %. For a 50-nm DNA strand (146 base pairs), the C^* varies moderately with the ionic strength of the aqueous solution from about 13 wt % in 0.01 M Na^+ to 17 wt % in 1 M Na^+ at 25 °C. Under the identical conditions, a fully grown, cholesteric LC phase occurs at 26 and 27 wt %, respectively. At further higher concentrations (33−38 wt %) in 0.1 M Na^+ a columnar hexagonal phase occurs in DNA solutions.[53] Generally, several parameters of a polyelectrolyte are expected to change with the ionic strength of the solution, namely the persistence length, q, and the effective diameter. Consequently, these parameters among others have a significant influence on C^*. Studies of the variation of C^* values for these viologen polymers with the increasing ionic strength are in progress and will be reported elsewhere.

Thermal Properties. The lyotropic solution in either EG or DEG for each of the polymers exhibited a broad endotherm in its DSC thermogram that corresponded to the transition from its lyotropic lamellar phase to the isotropic phase. These results were verified on heating the lyotropic solutions on the hot stage of a PLM under crossed polarizers at temperatures above the endothermic transitions by the observation of a dark field of view (isotropic phase). It is important to note that the solutions did not retransform from the isotropic phase to the lyotropic on cooling at a rate of either 3 or 5 °C/min. This observation was consistent with the fact that there was no cooling exotherm in each of the DSC thermograms. However, they retransformed into the lyotropic phase from the isotropic phase either on very slow cooling or on keeping the sample at room temperature for several hours. On retransforming into the lyotropic phase on standing, there was the development of either a bâtonnets texture or a mosaic texture, indicating the lamellar lyotropic phase.

Photochromic Properties. The lyotropic solutions of all of the viologen polymers in either glycerine or benzyl alcohol, on irradiation with UV light, produced a deep blue color. The UV−vis spectrum for such a deep blue solution of polymer **I-1** in glycerine is shown in Figure 12. The two absorption bands at 390 and 608 nm corresponded to the formation of a viologen cation radical moiety and a shoulder band at 568 nm to the dimeric cation radical, which are consistent with the reported values of this cation radical.[54] Interestingly enough, this deep blue color persisted in air for a long period of time. In other words, it is air-insensitive. Additionally, despite the development of deep blue color in its lyotropic solution, it retained its liquid crystalline phase as observed with the PLM studies. It is essential to mention here that this cation radical can be produced by the thermal reduction, chemical reduction, electrochemical reduction, and photoreduction of the viologen moiety. Thus generated, it is stable only in the absence of air because it reacts with dioxygen to revert back to the viologen moiety. Furthermore, in the photochemical reduction of a viologen moiety to generate this cation radical, it usually requires a photosensitizer such as tris(2,2′-bipyridyl)ruthenium(II) complex and a sacrificial donor such as ethylenediaminetetraacetic acid (EDTA).[55] Therefore, it was observed that the lyotropic solutions of these viologen polymers on simple irradiation with UV light underwent reduction to produce the deep blue color in the absence of both a photosensitizer and a sacrificial donor. This reduction occurred via the electron transfer from the tosylate ion to the viologen moiety, as is similar to the electron transfer from the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ion to the viologen that also produces a deep blue color.[56] The air insensitivity of this cation radical was related to the limited dioxygen diffusion through the viscous medium such as glycerine and benzyl alcohol. The photogeneration of this cation radical in the presence of air is an active area of research with the goal for efficient photochemical solar energy storage.[57,58] For example, the simplest way for the photogeneration of this cation radical may facilitate the photochemical reduction of water to yield hydrogen in the presence of a suitable catalyst such as colloidal platinum.[59] It is important to note that the UV−vis spectra of lyotropic solutions of these polymers in glycerine and benzyl alcohol showed red-shifted absorption bands at 302 and 358 nm, respectively, when compared with the model compound methyl viologen having chloride as a counterion (259 and 263 nm in water and methanol, respectively).[60]

Conclusions

A series of viologen polymers were prepared by the quaternization reaction of 4,4′-bipyridyl with either the ditosylate of *trans*-1,4-cyclohexanedimethanol or the mixtures of ditosylates of *trans*-1,4-cyclohexanedimethanol and 1,8-octanediol in various molar ratios in acetonitrile. Their chemical structures were determined by various experimental techniques including FTIR and 1D and 2D NMR spectroscopies. They showed the polyelectrolyte properties in a common organic solvent such as methanol. Although the literature is replete with many neutral lyotropic polymers of varied structures that require a wide variety of solvents ranging from concentrated H_2SO_4 to common organic solvents,[24,40,47,48] there exist relatively few ionic polymers that exhibit lyotropic properties in common organic solvents.[10,18,49] All of these viologen polymers exhibited lyotropic properties in many common organic solvents including methanol, ethanol, ethylene glycol, diethylene glycol, glycerine, and benzyl alcohol. Their lyotropic phase was of lamellar type that was determined by the observation of a bâtonnets texture or a polygonal arrays texture with the polarizing light microscope studies. Similar to nonionic lyotropic polymers, they formed isotropic solutions at low concentrations, at intermediate concentrations they exhibited biphasic solutions in which the coexistence of an anisotropic and an isotropic phase occurred, and at relatively high concentrations they formed fully grown lyotropic lamellar phases. Their critical concentrations were as low as 5 wt % and as high as 20−40 wt % in various alcohols. These results suggested that their critical concentrations were dependent on the polarity of the solvent, the hydrophobicity and hydrophilicity of the solvent, and the microstructure of the polymer chain. Copolymerization introduced irregularities in the polymer chains, decreased the crystallinity, and hence increased the solubility of these polymers in polar organic solvents. Consequently, the prospect for the formation of a lyotropic lamellar phase increased significantly. Therefore, the lyotropic properties of the present series of viologen polymers in various polar organic solvents in combination with their polyelectrolyte properties provided an extension to the field of LCPs, which are termed as LC polyelectrolytes. They may offer many potential applications. Some notable examples are the following: they can be used to enhance the miscibility with other carefully selected macromolecules through ionic interactions; they can provide an interesting subject of interaction between two LC polyelectrolytes of opposite charges, which has not been reported to date; and they may also provide a model system of interactions of various surfactants with LC polyelectrolytes in order to understand the self-assembly of viruses, membranes, or many more complex biological systems.[61]

Finally, the lyotropic solutions of these polymers in both glycerine and benzyl alcohol generated a deep blue solution on simply irradiation with UV light in the presence of air. This deep blue solution was due to the generation of a cation radical via electron transfer from the tosylate ion to the 4,4′-bipyridinium moiety, which was detected by the two characteristic absorption bands at 390 and 608 nm in the UV−vis spectrum. This procedure for generating the viologen cation radical is relatively a simpler one if one recalls that a typical procedure requires both a photosensitizer and a sacrificial donor, which may have practical implications for efficient solar energy storage.[55−57]

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References and Notes

(1) Rembaum, A.; Hermann, A. M.; Stewart, F. E.; Gutmann, F. *J. Phys. Chem.* **1969**, *73*, 513.
(2) Simon, M. S.; Moore, P. T. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1.
(3) Sato, H.; Tamamura, T. *J. Appl. Polym. Sci.* **1979**, *24*, 2075.
(4) Moore, J. S.; Stupp, S. I. *Macromolecules* **1986**, *19*, 1815.
(5) Merz, A.; Reitmeier, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 807.
(6) Hashimoto, T.; Kohjiya, S.; Yamashita, S.; Irie, M. *J. Polym. Sci., Polym. Chem. Ed.* 1**991**, *29*, 651.
(7) Cheng, P.; Subramanyam, S.; Clough, S. B.; Blumstein, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (1), 138.
(8) Cheng, P.; Subramanyam, S.; Blumstein, A. *Polym. Prepr., (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (3), 285.

(9) Blumstein, A.; Cheng, P.; Subramanyam, S.; Clough, S. B. *Makromol. Chem., Rapid Commun.* **1992**, *13,* 67.

(10) Cheng, P.; Blumstein, A.; Subramanyam, S. *Mol. Cryst. Liq. Cryst.* **1995**, *269,* 1.

(11) Jegal, J. G.; Blumstein, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (2), 120.

(12) Jegal, J. G.; Blumstein, A. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33,* 2673.

(13) Harris, F. W.; Chuang, K. C.; Huang, S. A. X.; Janimak, J. J.; Cheng, S. Z. D. *Polymer* **1994**, *35,* 4940.

(14) Han, H.; Bhowmik, P. K. *Trends Polym. Sci.* **1995**, *3,* 199.

(15) Han, H.; Bhowmik, P. K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36* (2), 330.

(16) Bhowmik, P. K.; Han, H. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33,* 1745.

(17) Bhowmik, P. K.; Akhter, S.; Han, H. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33,* 1927.

(18) 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.

(19) Han, H.; Bhowmik, P. K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (2), 856.

(20) Bhowmik, P. K.; Xu, W.; Han, H. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32,* 3205.

(21) Bhaskar, C.; Kops, J.; Marcher, B.; Spanggaard, H. In *Recent Advances in Liquid Crystalline Polymers;* Chapoy, L. L., Ed.; Elsevier: London, 1985; p 79.

(22) Thammongkol, V.; Warner, S. B.; Polk, M. B. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33,* 189.

(23) Osman, M. A. *Macromolecules* **1986**, *19,* 1824.

(24) Kwolek, S. L.; Morgan, P. W.; Schaefgen, J. R. In *Encyclopedia of Polymer Science and Engineering,* 2nd ed.; Mark, H. F., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1988; Vol. 9, p 1.

(25) Johns, W. F.; Lukes, R. M.; Sarett, L. H. *J. Am. Chem. Soc.* **1954**, *76,* 5026.

(26) Haggis, G. A.; Owen, L. N. *J. Chem. Soc.* **1953**, 404.

(27) Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1955**, *77,* 195.

(28) Cohen, J.; Priel, Z. *Macromolecules* **1989**, *22,* 2356.

(29) Scranton, A. B.; Rangarajan, B.; Klier, J. *Adv. Polym. Sci.* **1995**, *122,* 1.

(30) Wu, J.-L.; Wang, Y.-M.; Hara, M.; Granville, M.; Jérôme, R. J. *Macromolecules* **1994**, *27,* 1195.

(31) Berson, A.; Lindgren, J. *Solid State Ionics* **1993**, *60,* 37.

(32) Frech, R.; Huang, W. *Macromolecules* **1995**, *28,* 1246.

(33) Dissanayake, M. A. K. L.; Frech, R. *Macromolecules* **1995**, *28,* 5312.

(34) Lowry, S. R.; Mauritz, K. A. *J. Am. Chem. Soc.* **1980**, *102,* 4665.

(35) Cable, K. M.; Mauritz, K. A.; Moore, R. B. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33,* 1065.

(36) Sander, B.; Tübke, J.; Wartewig, S.; Shashkov, S. *Solid State Ionics* **1996**, *83,* 87.

(37) Stevens, M. J.; Kremer, K. *J. Chem. Phys.* **1995**, *103,* 1669.

(38) Donald, A. M.; Windle, A. H. *Liquid Crystalline Polymers;* Cambridge University: Cambridge, U.K., 1992.

(39) Itou, T.; Teramoto, A. *Macromolecules* **1984**, *17,* 1419.

(40) Moucharafieh, N.; Friberg, S. E. *Mol. Cryst. Liq. Cryst. (Lett.)* **1979**, *49,* 231.

(41) Decher, G.; Ringsdorf, H. *Liq. Cryst.* **1993**, *13,* 57.

(42) Preston, J. *Angew. Makromol. Chem.* **1982**, *109/110,* 1.

(43) Han, H.; Bhowmik, P. K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (2), 619.

(44) El-Nokaly, M.; Friberg, S. E.; Larsen, D. W. *J. Colloid Interface Sci.* **1984**, *98,* 274.

(45) Rosevear, F. B. *J. Am. Oil Chem. Soc.* **1954**, *31,* 628.

(46) Candau, F.; Ballet, F.; Debeauvais, F.; Wittmann, J.-C. *J. Colloid Interface Sci.* **1982**, *87,* 356.

(47) *Polymeric Liquid Crystals;* Blumstein, A., Ed.; Plenum: New York, 1985.

(48) *Liquid Crystallinity in Polymers Principles and Fundamental Properties;* Ciferri, A., Ed.; VCH: New York, 1991.

(49) Lin, J.; Sherrington, D. C.; Nield, E.; Richards, R. W. *Macromolecules* **1992**, *25,* 7107.

(50) Stroobants, A.; Lekkerkerker, H. N. W.; Odijk, T. *Macromolecules* **1986**, *19,* 2232 and references therein.

(51) Oster, G. *J. Gen. Physiol.* **1950**, *33,* 445.

(52) Wen, X.; Meyer, R. B.; Caspar, D. L. D. *Phys. Rev. Lett.* **1989**, 63, 2760.

(53) Livolant, F.; Leforestier, A. *Prog. Polym. Sci.* **1996**, *21,* 1115.

(54) Thompson, M. E.; Snover, J. L. *J. Am. Chem. Soc.* **1994**, *116,* 765 and references therein.

(55) Takuma, K.; Shuto, Y.; Matsuo, T. *Chem. Lett.* **1978**, 983.

(56) Nagamura, T. *Pure Appl. Chem.* **1996**, *68,* 1449.

(57) Dai, S.; Sigman, M. E.; Burch, E. L. *Chem. Mater.* **1995**, *7,* 2054.

(58) Iyere, P. A. *Chem. Mater.* **1995**, *7,* 2224.

(59) Kiwi, J.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101,* 7214.

(60) Kaneko, M.; Yamada, A. *Makromol. Chem.* **1981**, *182,* 1111.

(61) Ciferri, A. *Macromol. Chem. Phys.* **1994**, *195,* 457.

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