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# Determination of the Molecular Parameters and Studies of the Chain Conformation of Polybenzimidazole in DMAc/LiCl

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ABSTRACT: Static light scattering has been used for the first time to obtain the molecular parameters and to study the chain conformation of a previously synthesized *m*-polybenzimidazole (*m*-PBI) sample in *N*,*N*-dimethylacetamide (DMAc) with 4% (g/mL) LiCl. A weight-average molecular weight $M_w = 199\,200$ g/mol; radius of gyration $R_g = 44.0$ nm and $A_2 = 0.0022$ cm$^3$ mol/g$^2$ are reported. The chain conformation of *m*-PBI was studied as a function of (a) polymer concentration (0.1−20 mg/mL) at a fixed salt concentration of 4% LiCl and (b) salt concentration (0.05−7%) at a fixed polymer concentration of 0.3 mg/mL. As polymer or salt concentration was increased, the chains collapsed initially, and then underwent fluctuations in size without a significant decrease in their average size. The collapse was associated with a conformational transition from random coil to an "extended wormlike" chain at increasing polymer concentration. At polymer concentrations greater than 9 mg/mL, the average size of the polymer chain was relatively constant at 31.2 ± 1.7 nm. Reduced viscosity measurements indicated that *m*-PBI behaved like a polyelectrolyte in the presence of DMAc/LiCl. Circular dichroism measurements confirmed the conformational transitions observed from light scattering by indicating the presence of optical activity at polymer concentrations above 2 mg/mL. Birefringence measurements at polymer concentrations between 4 and 25 mg/mL indicated the presence of possible relaxation caused both by the degree of chain flexibility and by deformation in polymer chains due to the influence of the laser intensity. These results contribute to our overall understanding of chain stiffness and conformational transitions in PBI polymers, which may play an important role in the preparation of polymer electrolyte membranes (PEMs) via sol−gel processing.

## Introduction

Polybenzimidazoles are a class of thermally stable polymers that have been commercially developed as textile fibers, high-temperature matrix resins, adhesives, and foams. The polymer, poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole]) (*m*-PBI), was commercialized by the Celanese Corporation in 1983 and is widely used in firefighters protective clothing, high-temperature gloves, and astronaut flight suits due to its excellent chemical and thermal stability.[1] Additionally, polybenzimidazoles have emerged as promising candidates for low-cost and high performance membranes for high-temperature fuel cells.[2−4] These membranes can operate reliably at temperatures above 120 °C without humidification, thus offering many advantages such as fast electrode kinetics, high tolerance to fuel impurities such as carbon monoxide, and greatly simplified system design.[5] Preliminary results have been reported by Helminiak et al.[6] on solution properties of low molecular weight *m*-PBI such as intrinsic viscosity behavior as a function of temperature and LiCl salt concentrations in *N*,*N*-dimethylacetamide (DMAc), as well as molecular parameters such as number-average molecular weight, $M_n$, and second virial coefficient, $A_2$, obtained by osmotic pressure measurements. Surprisingly, absolute molecular weights (i.e., weight-average molecular weight, $M_w$) and other molecular parameters such as radius of gyration, $R_g$, have not been measured for this commercially important polymer using static light scattering techniques. In addition, while previous studies on the solution properties of other types of polybenzimidazoles in *N*,*N*-dimethylacetamide (DMAc) have focused on obtaining their molecular parameters, intrinsic viscosity, and hydrodynamic chain dimensions[7] as well as on understanding their molecular aggregation in solution,[8] no detailed studies have been done to improve our understanding of the chain conformation of these polymers in solution. Although it can be inferred from prior studies by Benicewicz and co-workers[9] that a sol−gel transition leads to a variation in the morphology of the sol−gel membrane (based on different chemical structures) for polybenzimidazoles, knowledge of the chain conformation of this polymer in solution could have an impact on these variations in morphology. In addition, the morphology of the sol−gel membrane may also influence the proton conductivity and mechanical properties of these membranes for fuel cell applications.

In this paper, we report the molecular parameters and chain conformation behavior for the first time of high-molecular-weight *m*-PBI (based on inherent viscosity measurements). Our results from molecular parameters, i.e., $M_w$ and $R_g$, confirm the synthesis of high-molecular-weight *m*-PBI. Polymer chain conformation was studied by using viscosity measurements and static light scattering techniques, which involved varying polymer or salt concentrations. Reduced viscosity measurements as a function of varying polymer concentration indicated that the polymer behaved like a polyelectrolyte in solution and conformational changes occurred at increasing concentrations. Light scattering studies showed that varying the polymer or salt concentration led to a conformational transition in the polymer chain from a random coil or wormlike chain to an "extended wormlike" chain. Furthermore, the presence of optical activity obtained from circular dichroism measurements was linked to

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this conformational transition, which occurred at higher polymer concentrations. Birefringence measurements indicated the possibility of relaxation caused by the degree of chain flexibility and by deformation in the polymer chains due to the influence of laser intensity. These results will contribute to our understanding of the possible formation of associating structures at high polymer concentrations and may be applicable to elucidating the role of solution conformational behavior on membrane formation processes.

## Experimental Section

The *m*-PBI sample with inherent viscosity of 1.59 dL/g (measured in 96% sulfuric acid at a concentration of 0.2 g/dL) was prepared by polymerization of isophthalic acid (Amoco, 99+%) and 3,3′,4,4′-tetraaminobiphenyl (Celanese, polymerization grade) in polyphosphoric acid as reported previously.[9] The sample was dried for 1 h at 105 °C in a vacuum oven prior to use. The solvent mixture was prepared by dissolving 4% LiCl (dried at 105 °C overnight in a vacuum oven prior to use) (anhydrous, 99+%, Acros Organics) in *N*,*N*-dimethylacetamide (DMAc) (spectrophotometric grade, 99+%, Acros Organics).

For FT-IR measurements, we prepared *m*-PBI (1.59 dL/g) films by dissolving the polymer in dimethylacetamide/lithium chloride solvent mixture (DMAc/4% LiCl). The solution obtained was then poured and cast on a Teflon dish. The solvent was evaporated at 100 °C for 5 h in a vacuum oven. The film obtained was then rinsed with DI−water a few times to remove any LiCl and residual DMAc was extracted by heating at 200 °C for 2 h. Pieces of yellow films with thickness in the range of 100−120 $\mu$m were obtained and stored. Prior to FT-IR measurements, film samples were dried at 100 °C for 1 h.

For static light scattering and viscosity measurements, we prepared *m*-PBI solutions individually at different polymer concentrations by mixing the appropriate amounts of polymer with the solvent mixture in 22 mL screw thread capped glass vials (Fisher Scientific). The desired polymer concentrations were first stirred at room temperature for at least 1 h in the capped vials and then heated in an oil-bath (with gentle stirring) at 120 °C for at least another hour until complete dissolution of the polymer was observed with no noticeable aggregates. The solutions were removed from the oil-bath, the vial caps were then tightened, and the vials were allowed to cool to room temperature. Solutions for all experiments were filtered through Whatman disposable syringe filters (PTFE filter media with polypropylene housing, 13 mm diameter, 0.2 $\mu$m pore size) into glass vials that had been acetone-rinsed and dried. All measurements were performed within 3−5 days of solution preparations.[8,10] This was necessary to allow for equilibrium of the solutions.

Viscosity measurements were performed at 30.0 °C using No. 75 Cannon-Ubbelohde viscometers. Measurements were made in the range of polymer concentration from 0.1 to 1.8 mg/mL, which included the domain over which the light scattering experiments were performed. A minimum of four readings were taken and averaged for the final flow time for each polymer concentration.

Static light scattering measurements were performed in the "batch-mode" with a Brookhaven Instruments Corporation (BIC) molecular weight analyzer (BI-$M_w$A). A nominal 30 mW, vertically polarized laser with $\lambda = 660$ nm was used as the light source. All light scattering measurements were made at 30.0 °C. Intensity measurements were performed between 35 and 145° for a total of seven scattering angles, $\theta$. The light scattering apparatus was calibrated using filtered toluene in order to obtain the Rayleigh ratio, and the apparatus was then normalized with a polystyrene/THF solution.

The refractive index, $n$, of the DMAc-4% LiCl solvent mixture was determined at 30.0 °C using a Leica Abbe Mark II refractometer. The value obtained was $n = 1.4486$ at an extrapolated wavelength of $\lambda = 660$ nm.[11] The refractometer was calibrated using water as the reference standard ($n = 1.3325$ at $\lambda = 589$ nm, 25.0 °C). The refractive index increment ($dn/dc$) of the polymer solution was determined at 30.0 °C using a WGE Dr. Bures Differential refractometer at a fixed wavelength of $\lambda = 620$ nm and a source intensity of 80%. The refractive index increment value ($dn/dc$) obtained for the polymer sample was 0.3072 mL/g. A depolarization ratio ($\rho_v$) of 0.006 was measured for the sample using a BI-200 SM goniometer research system.

The Fourier transform infrared (FTIR) spectrum was recorded on a Perkin-Elmer Paragon 500 spectrometer. The spectrum was obtained in the transmission mode from a film cast sample using DMAc/4% LiCl. The range of scan was from 4000 to 400 cm$^{-1}$ at a resolution of 1 cm$^{-1}$ with an average of 16 scans.

Circular dichroism spectra were recorded at 25.0 °C with a Jasco J-715 spectropolarimeter in the wavelength range of 250−500 nm using a 0.01 mm detachable quartz cell. An average of three spectra was obtained.

Birefringence measurements were performed using a simple setup in the laboratory at 25.0 °C. A beam of light from a 13 mW He−Ne laser ($\lambda = 632.8$ nm) was directed through a horizontal Glan Taylor calcite prism polarizer (analyzer) and then through the sample. The sample was housed in a standard rectangular cell, which was made from optical glass with a path length of 2 mm and mounted on an adjustable rectangular holder. The exiting beam of light from the sample, passed through a second polarizer at crossed polars to the first analyzer and then finally to a detector. The ratio of the intensity of the exiting beam, $I$, to that of the beam incident on the sample, $I_o$, represents the birefringence.

Information on polymer−solvent interactions was determined by making a plot of reduced viscosity ($\eta_{sp}/c$) vs various polymer concentrations. The equation for obtaining the reduced viscosity is shown below:

$$\eta_{red} = \eta_{sp}/c \qquad (1)$$

where $\eta_{red}$ is the reduced viscosity, $c$ is the polymer concentration, and $\eta_{sp}$ is the specific viscosity which is given by $\eta_{sp} = (\eta\text{-}\eta_s)/\eta_s$, with $\eta$ and $\eta_s$ being the viscosity of the solution and the solvent, respectively.

Molecular parameters obtained from static light scattering were determined by using a Zimm plot analysis. The equation representing a Zimm plot is shown below:

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{M_w}\left(1 + \frac{q^2 R_g^{\,2}}{3}\right) + 2A_2 c \qquad (2)$$

where $K$ is the optical constant which is given by $K = 4\pi^2 n^2 (dn/dc)^2/(N_A \lambda^4)$, $n$ is the refractive index of the solvent, $\lambda$ is the wavelength of light in the vacuum, $dn/dc$ is the specific refractive index increment of the solution, $N_A$ is Avogadro's number, $M_w$ is the weight-average molecular weight, $A_2$ is the second virial coefficient, $\Delta R_\theta$ is the excess Rayleigh ratio, and $q$ is the magnitude of the scattering wave vector: $q = (4\pi n/\lambda)\sin(\theta/2)$ where $\theta$ is the scattering angle. In our experiments, the scattering angle $\theta$ was varied between 35 and 145°, which corresponds to scattering wave vectors $q$ in the range in the range $8.8 \times 10^{-4}$ to $2.8 \times 10^{-3}$ Å$^{-1}$.

A Guinier plot represented by eq 3 below was used to obtain the size ($R_g$) of the polymer molecules in solution:

$$I_{ex}(q) = C_1 \exp(-R_g^{\,2} q^2/3) \qquad (3)$$

A plot of $\ln(I_{ex}(q))^{-1}$ vs $q^2$ yields a straight line when a Guinier plot is appropriate, from which the slope, $R_g$ is obtained. In this plot, $I_{ex}$ is the excess intensity of scattered light and $C_1$ is a constant. The Guinier equation above is acceptable only when $qR_g \le 1$, thus its use to evaluate $R_g$ is valid only when the extrapolation of experimental data is over a range of $\theta$ for which $R_g \le q^{-1}$.

A partial Zimm plot, used to obtain size information about small molecules in solution is represented by eq 4:

$$(I_{ex}(q))^{-1} = C_2[1 + (R_g^{\,2} q^2/3)] \qquad (4)$$

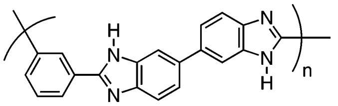

**Figure 1.** Chemical structure of poly [2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] (*m*-PBI).

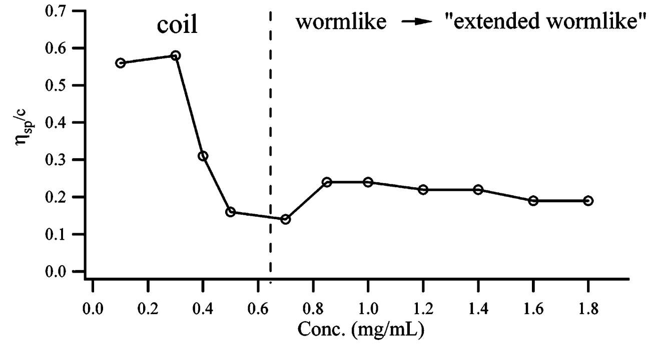

**Figure 2.** Reduced viscosity, $\eta_{sp}/c$ , as a function of various polymer concentrations for *m*-PBI (1.59 dL/g) in DMAc/4% LiCl. The line is drawn as a visualization aid. Errors are within the size of the points.

In this plot, $R_g$ is determined from the slope and intercept of a plot of $(I_{ex}(q))^{-1}$ vs $q^2$ and $C_2$ is a constant.

A partial Berry plot, used to obtain size information about large molecules in solution is represented by eq 5:

$$(1/\,(I_{ex}(q))^{1/2} = C_3(1 + (R_g{}^2q^2/6) \qquad (5)$$

Here, $R_g$ is determined from the slope and intercept of a plot of $(1/(I_{ex}(q))^{1/2}$ vs $q^2$ and $C_3$ is a constant.

The shape analysis of the polymer chains was obtained using a Kratky plot, which is given by eq 6:

$$I_{ex}(q)q^2 \text{ vs } q \qquad (6)$$

Plotting $I_{ex}(q)q^2$ vs $q$ yields different shapes depending on the structure of the polymer chain.

## Results

The chemical structure of the polymer, poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] (*m*-PBI), used in this work is shown in Figure 1. This polymer is often described as semiflexible in nature due to the orientation of the *m*-phenylene ring and the rotation that can occur around the single bonds in the backbone structure. An FTIR spectrum of the dry *m*-PBI film (not shown) in the region of 4000−400 cm$^{-1}$ was obtained. The typical absorption bands obtained were in agreement with previously recorded *m*-PBI spectra.[12] They are as follows: near 800 cm$^{-1}$ (imidazole C−H out-of-plane bending, overlapped by benzene aromatic skeletal absorptions), near 1300 cm$^{-1}$ (imidazole C−N stretching), near 1450 cm$^{-1}$ (imidazole C−N in-plane vibration), and near 1620 and 1510 cm$^{-1}$ (combined C=C and C=N ring vibration).

A reduced viscosity plot ($\eta_{sp}/c$) vs various polymer concentrations of *m*-PBI in DMAc/4% LiCl is shown in Figure 2. The viscosity behavior shown in this figure is typical of polyelectrolyte solutions,[13−16] whereby a maximum is observed on the addition of a salt (LiCl) and the presence of a sharp increase in reduced viscosity at decreasing polymer concentration. We observed a gradual increase in the reduced viscosity at decreasing concentrations (1.8−0.85 mg/mL) followed by a slight decrease in viscosity (0.85−0.7 mg/mL), and then finally a sharp increase in reduced viscosity (0.5−0.3 mg/mL) with the appearance of a maximum near 0.3 mg/mL. The observation of a maximum at low polymer concentrations has been shown to occur for polyelectrolytes in nonaqueous systems containing low salt concentrations.[15,16]

Figure 3 shows typical Zimm plots for a *m*-PBI sample in DMAc/4% LiCl with an inherent viscosity (IV) of 1.59 dL/g. The top Zimm plot (a) shows all seven measured scattering angles, while the bottom Zimm plot (b) shows all measured angles except for 50°. Because of systematic error in instrument normalization, removal of data at 50° did not significantly alter the values of molecular parameters obtained compared to the inclusion of the angle. Table 1 shows the tabulated molecular parameters ($M_w$, $R_g$, and $A_2$) obtained from the Zimm plot for the *m*-PBI sample measured at all seven scattering angles. Molecular parameters obtained represent an averaged value from several trials.

Figure 4 shows a plot of the $R_g$ values of *m*-PBI in DMAc/4% LiCl as a function of varying polymer concentration (0.1−20.0 mg/mL). From this plot, it was observed that at increasing polymer concentrations, the average size of the polymer chain sharply collapsed (0.1−4 mg/mL), and then experienced fluctuations in average size (4−10 mg/mL). At concentrations in the range of 10 to 20 mg/mL, the average size of the polymer chains remained relatively constant at 31.2 ± 1.7 nm. $R_g$ values were obtained using a Guinier plot analysis because this plot gave values with the lowest order-of-error fit when compared to values obtained using the partial Zimm and Berry plots.

Kratky plots of *m*-PBI with polymer concentrations in the range 0.1−20.0 mg/mL are shown in Figure 5. In these plots, we observed that the polymer chain conformation changed from a flexible/random coil (at concentrations less than 0.6 mg/mL) to a wormlike chain (at concentrations between 0.6 and 4.0 mg/mL) and finally to an “extended wormlike” chain at concentrations in the range of 4.0 to 20.0 mg/mL.

Figure 6 shows a similar plot of the $R_g$ values of *m*-PBI as a function of varying salt concentration (0.05 to 7.0%). From the plot, we observed a gradual decrease with slight fluctuations in the average size of the polymer chains with increasing salt concentration until a minimum of 31.0 nm was obtained using 4% LiCl salt. Above 4% LiCl, further fluctuations in the average size of the polymer chains were observed. Polymer concentrations of the samples were fixed at 0.3 mg/mL. A Guinier plot analysis similar to the one mentioned earlier was used to fit the data. Table 2 shows the ranges of salt concentrations studied, as well as the corresponding $R_g$ values obtained.

Kratky plots of *m*-PBI at varying salt concentrations are shown in Figure 7. As salt concentration increased from 0.05% to 7.0% LiCl, polymer chain conformation changed from a wormlike to an “extended wormlike” chain. This change in polymer chain conformation was very similar to that observed when the polymer concentration was varied above 0.6 mg/mL.

Figure 8 shows the circular dichroism spectra of *m*-PBI solutions with varying polymer concentrations from 0.4 to 25 mg/mL in DMAc/4% LiCl. On the basis of these spectra, it was observed that there was no clear indication of a defined structure (i.e., no optical activity) at concentrations of 0.4, 1.0, and 2.0 mg/mL. However, at concentrations in the range of 4.0 to 25.0 mg/mL, the formation of a defined structure (i.e., presence of optical activity) at wavelength ranges between 280 and 390 nm was clearly observed. Previous studies have indicated that PBI in DMAc absorbs at a wavelength close to 350 nm.[8] This absorption peak was observed at polymer concentrations above 2.0 mg/mL with the appearance of multiple, broad and sharp peaks observed at this wavelength regime as polymer concentration was increased.

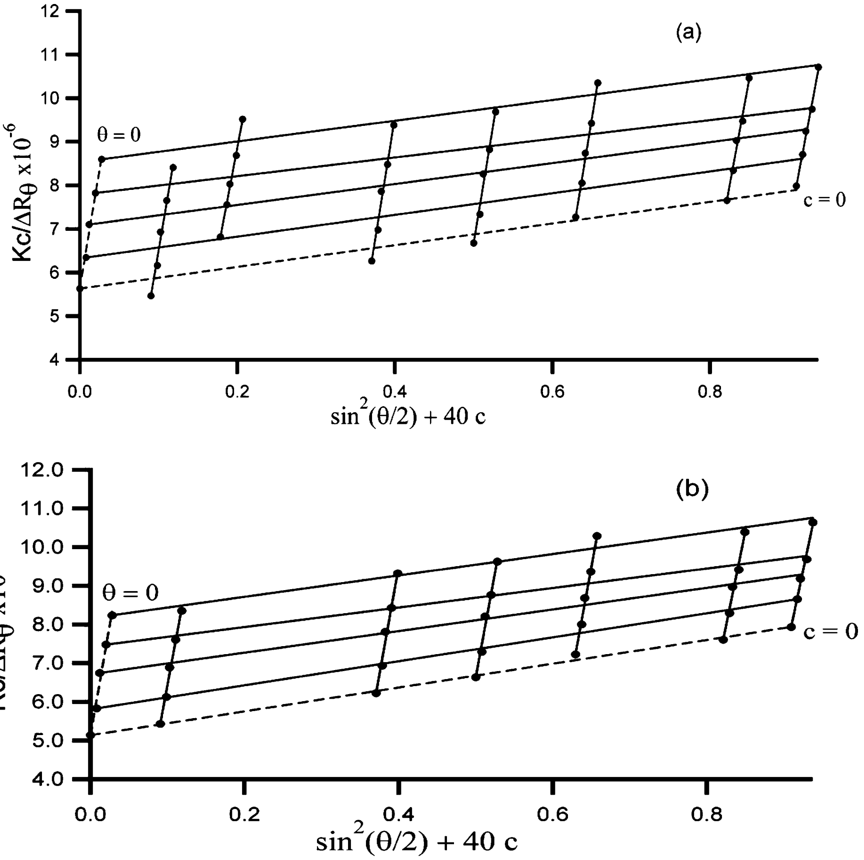

**Figure 3.** (a). Zimm plot for *m*-PBI (IV. 1.59 dL/g) in DMAc/4% LiCl. Concentrations of solutions: $c_1 = 0.2$ mg/mL; $c_2 = 0.3$ mg/mL; $c_3 = 0.5$ mg/mL; $c_4 = 0.7$ mg/mL. Range of scattering angles measured: 35−145°. (b). Zimm plot for *m*-PBI (IV. 1.59 dL/g) in DMAc/4% LiCl. Concentrations of solutions: $c_1 = 0.2$ mg/mL; $c_2 = 0.3$ mg/mL; $c_3 = 0.5$ mg/mL; $c_4 = 0.7$ mg/mL. Range of scattering angles measured: 35°-145°. Angle at 50° removed.

**Table 1. Molecular Parameters for *m*-PBI (1.59 dL/g) in DMAc/4% LiCl**

| sample[a] | $M_w$[b] ( $\times 10^{-5}$) | $A_2$ ( $\times$ $10^{-3}$), ($cm^3$•mol)$g^2$ [c] | $R_g$,[d] nm | $\rho_v$ |
|---|---|---|---|---|
| *m*-PBI | 1.99 ± 0.14 | 2.18 ± 0.38 | 43.9 ± 3.6 | 0.006 |

[a] Inherent viscosity of sample measured in 96% $H_2SO_4$ at a concentration of 0.2 g/dL. [b] Average molecular weight values obtained. [c] Average second virial coefficient values obtained. [d] Average radius of gyration values obtained.

Figure 9 shows birefringence measurements for polymer concentrations in the range of 0.4 to 30 mg/mL at a fixed 4% LiCl concentration. It was observed that at polymer concentrations less than 4.0 mg/mL (i.e., flexible/random coil and wormlike regime), there was very little or no birefringence observed. However, at concentrations in the range of 4.0 to 20 mg/mL (i.e., "extended wormlike" regime), 25 and 30 mg/mL, birefringence was observed. There was also a clear indication of positive birefringence occurring at concentrations of 4, 13, and 30 mg/mL. All other concentrations above 4 mg/mL displayed negative birefringence.

## Discussion

The chemical structure of *m*-PBI, shown in Figure 1, contains catenation angles between 120 and 150° [17] and is generally described as semiflexible in nature. In addition, due to the presence of the flexibility in the main chain, polymers in this category usually have multiple points of bond rotation and often show amorphous properties.[17] On the basis of the structure, it is possible for both inter and intramolecular hydrogen bonding to occur between the lone pair of electrons on nitrogen attached to one five membered ring −N= (proton acceptors) and the hydrogen on an adjacent five membered ring −N(H)− (proton donors). Our preliminary theoretical calculations for the ranges of the persistence length of the polymer chain using the wormlike-chain model gave values between 5 and 8 nm. This range of values are comparable to persistence lengths reported for polysaccharides such as corn amylose (3.26 nm)[18] and for *κ*-carrageenan (6.8 nm),[19] both of which are semiflexible polymers.

The addition of LiCl to *m*-PBI/DMAc solution was necessary in order to facilitate the breakup of aggregates as well as enhance the solubility of the polymer in the solvent. It has been reported by Helminiak et al.[6] that DMAc−LiCl is a better solvent for *m*-PBI than DMAc alone based on intrinsic viscosity studies. Addition of lithium chloride to the polymer solution has also been shown to increase the solubility of the polymer.[20] Since DMAc possesses hydrogens that cannot engage in hydrogen bonding, anions cannot be solvated. These "naked anions" will therefore be unencumbered by a layer of solvent molecules and will be highly active as nucleophilic bases.[21] This will allow the $Cl^-$ anions greater freedom to disrupt the inter- and intramolecular hydrogen bonds in *m*-PBI.

Previous studies have shown that there is an interaction between the LiCl salt when added to DMAc (a polar aprotic solvent). For instance, infrared spectra studies performed by Panar and Beste on amide solvents showed the formation of a new absorption band in the spectrum of DMAc when LiCl was added.[22] Also, $^{13}C$ NMR studies of the chemical shifts of carbonyl carbons of *N*,*N*-disubstituted amides have shown that there was a shift in the carbonyl carbon resonances toward lower frequencies upon addition of LiCl to these solvents.[23] On the basis of the results from infrared and NMR experiments, the

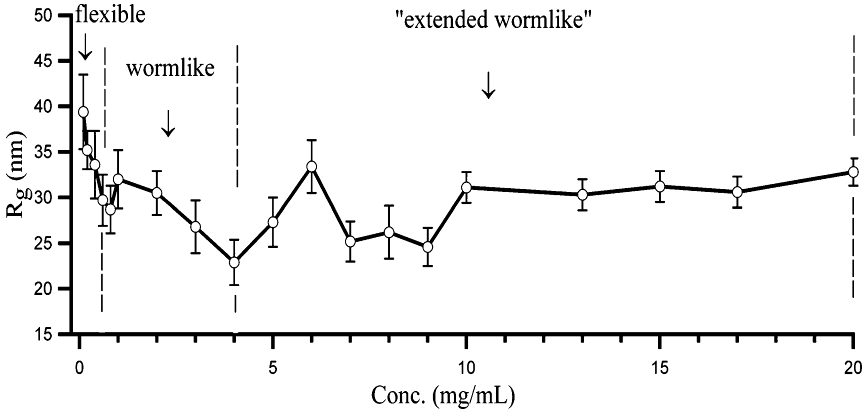

**Figure 4.** $R_g$ of *m*-PBI (1.59 dL/g) as a function of polymer concentration at fixed salt concentration (4% of LiCl). Error bars indicate noise in the measurements.

concept of a [DMAc + Li]$^+$ macrocation emerged, in the form of an ion−dipole complex, whereby the lithium cation was postulated to be located adjacent to the carbonyl oxygen of DMAc.[24,25] It has been shown that this postulation is consistent with decreases in the $^{13}$C NMR for spin−lattice relaxation time ($T_1$) of the DMAc carbons on addition of LiCl [26] and with reports of increases in viscosity in DMAc when LiCl was added.[27]

The presence or addition of LiCl salt as a "third component" in the PBI-DMAc solution can be viewed as a binary system. Thus far, it is clear that the addition of LiCl to DMAc forms a complex. Conductivity studies on PBI-DMAc−LiCl solutions performed by Hanley et al.[28] indicated that the presence of PBI reduced the conductivity of a DMAC−LiCl solution compared to the pure DMAc−LiCl system and this reduction varied directly with the amount of PBI present. The authors further explained that the polymer does not attach itself to all the available LiCl, even at dilute LiCl concentrations and that PBI and DMAc compete for the existing LiCl, with neither being strong enough to attract all the LiCl, thereby viewing the system as a two component system containing a PBI−LiCl system and DMAc−LiCl system.[28] Further evidence of the formation of a PBI−LiCl system can be inferred from the work of Federov et al.[29] on substituted benzanilides. The authors indicated that there is a direct interaction of Cl$^-$ anions with the protons of the amide group (NH) of substituted benzanilides in a DMAc−LiCl system, which causes strong chemical shifts in the NMR spectra of the NH proton. This interaction of the Cl$^-$ ions with the NH protons of the substituted benzanilides is analogous to the interaction of the Cl$^-$ ions with the NH protons of polybenzimidazoles.

A plot of reduced viscosity vs varying polymer concentration (0.1−1.8 mg/mL) for *m*-PBI in DMAc/4% LiCl (Figure 2) indicated that the polymer behaved like a polyelectrolyte in solution. Previous authors have also indicated polyelectrolyte behavior for polybenzimidazole in various solvents. Helminiak et al.[6] showed that for a low molecular weight polybenzimidazole, a plot of intrinsic viscosity (ranging from 0.792 to 1.495 dL/g) vs various LiCl concentrations (ranging from 0 to 2.5%) in DMAc was not linear due to an interaction of the polymer with the salt, which caused the polymer to behave like a polyelectrolyte. Kojima has shown based on viscosity studies that PBI in formic acid possesses the properties of a polyelectrolyte.[8] The present results in this paper showed that by fixing the LiCl salt concentration at 4.0% and varying the polymer concentration, a nonlinear behavior in the plot of reduced viscosity vs polymer concentration was also observed. Thus, our results on the polyelectrolyte behavior of *m*-PBI in solution are consistent with these previous results.

It was observed from our polyelectrolyte behavior of *m*-PBI in solution that a maximum in reduced viscosity occurred when polymer concentration was increased from 0.1 to 0.3 mg/mL. Additional increases in polymer concentration (0.3−0.5 mg/mL) resulted in a sharp decrease in the reduced viscosity, followed by a slight increase in reduced viscosity (0.7−0.85 mg/mL) and finally a gradual decrease in viscosity (0.85−1.8 mg/mL). This trend in polyelectrolyte behavior was linked to a conformational transition. For instance, Eisenberg and Katchalsky observed conformational transitions from reduced viscosity measurements of fractions of poly(methacrylic acid) (PMA) (a polyelectrolyte) in aqueous solution at various concentrations as a function of pH (degree of ionization).[30] The authors observed a gradual increase in reduced viscosity followed by sharp increase at pH above 6 with the appearance of a maximum when polymer concentration was decreased (1.72−0.11 mg/mL). They attributed this conformational transition from a hypercoiled molecule possessing a compact impermeable form (pH 2−3), to a randomly coiled form (pH 3−4) and finally to an extended rodlike structure (pH 4−8) as the degree of ionization or pH was increased. However, for our polybenzimidazole in DMAc/LiCl, a conformational transition from an expanded random coil to a compact chain was observed as polymer concentration was increased from 0.1 to 1.8 mg/mL. These differences in chain behavior for both polymers could be a due to differences in the stiffness of the polymer chains, hydrogen bonding interactions between the polymer and solvent as well as between the polymer chains. Our light scattering results on the size and shape of *m*-PBI in solution supports the conformational transition observed from viscosity measurements.

The sharp decrease in reduced viscosity observed at increasing polymer concentration (0.3−0.5 mg/mL) could be due to the screening effect of the LiCl in preventing hydrogen-bonding interactions between the polymer chains, which resulted in a collapse of the polymer chain. When polymer concentration was further increased (0.85−1.8 mg/mL), reduced viscosity gradually decreased due to a compaction of the polymer chain. In the reverse scenario, at decreasing polymer concentrations (1.8−0.85 mg/mL), we observed that the reduced viscosity gradually increased which indicated that the polymer chain was becoming less compact. However, at concentrations between 0.5 and 0.3 mg/mL, we observed an abrupt increase in reduced viscosity, which indicated that the polymer chain expanded forming a random coil structure.

Molecular parameters (Table 1) obtained from Zimm plots of the currently studied *m*-PBI (1.59 dL/g) (Figure 3) and of another *m*-PBI sample with an inherent viscosity of 1.18 dL/g

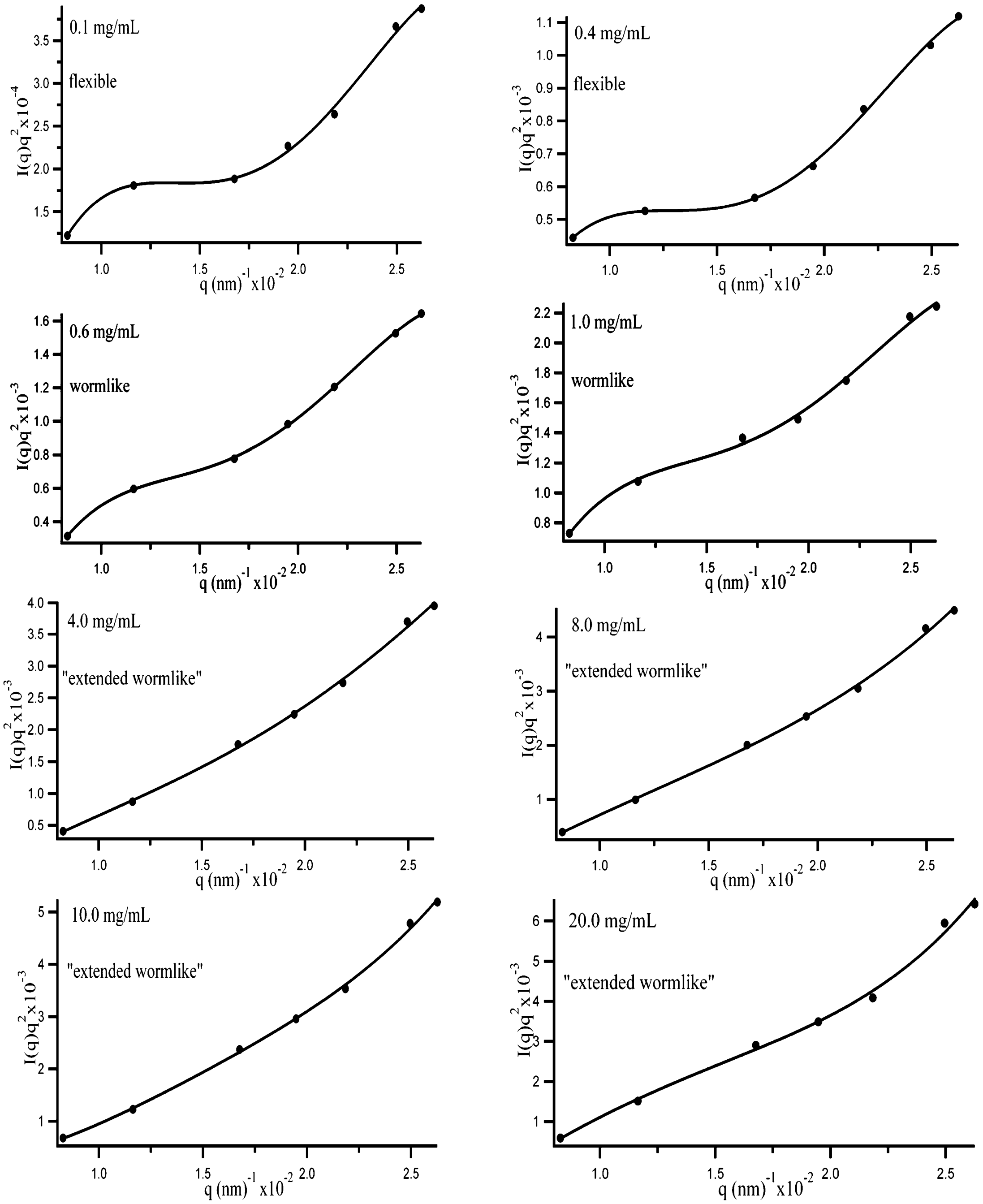

**Figure 5.** Kratky plots of *m*-PBI (1.59 dL/g) at different polymer concentrations in DMAc/4% LiCl.

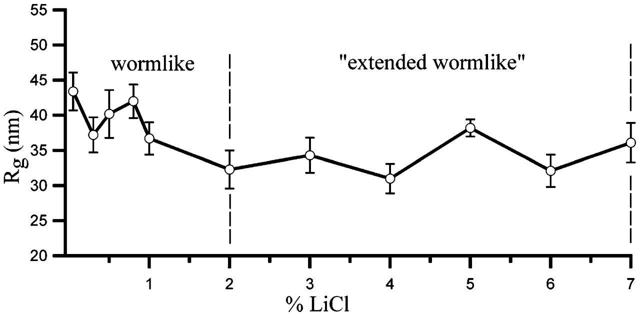

**Figure 6.** $R_g$ of *m*-PBI (1.59 dL/g) as a function of % LiCl concentration at fixed polymer concentration (0.3 mg/mL). Error bars indicate noise in the measurements.

agree well with their measured inherent viscosities (IV) in concentrated sulfuric acid. For instance, *m*-PBI (1.59 dL/g) with a weight-average molecular weight ($M_w$) of 199 200 g/mol and a radius of gyration ($R_g$) of 44.0 nm is greater than *m*-PBI (1.18 dL/g) with molecular parameters of 175 000 g/mol and 38.5 nm.

**Table 2. $R_g$ Values Obtained from Guinier Plots by Fixing Polymer at 0.3 mg/mL While Varying the Percent LiCl Salt Concentration at 30.0 °C**

| % LiCl | $R_g$, nm |
|---|---|
| 0.05 | 43.4 ± 3.6 |
| 0.3 | 37.2 ± 3.2 |
| 0.5 | 41.2 ± 5.1 |
| 0.8 | 42.0 ± 2.9 |
| 1.0 | 36.7 ± 2.6 |
| 2.0 | 32.3 ± 3.2 |
| 3.0 | 34.3 ± 3.5 |
| 4.0 | 31.0 ± 2.3 |
| 5.0 | 38.2 ± 1.6 |
| 6.0 | 32.1 ± 2.4 |
| 7.0 | 36.1 ± 3.0 |

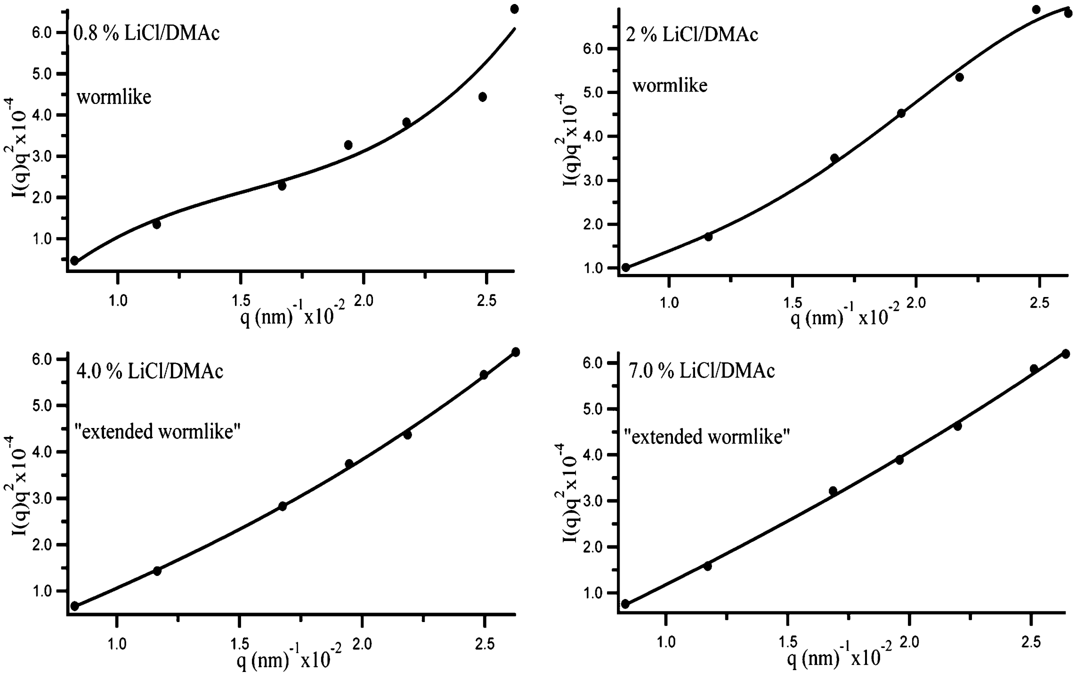

**Figure 7.** Kratky plots of *m*-PBI (1.59 dL/g) at varying salt concentrations in 0.3 mg/mL polymer concentration.

To study the effect of both polymer and salt concentrations on the average size ($R_g$) and shape (chain conformation) of *m*-PBI (1.59 dL/g) in DMAc/4% LiCl, it was necessary to first obtain its size distribution in the solvent mixture. Guinier, partial Zimm and partial Berry methods were all employed in obtaining the size distribution of PBI molecules. On the basis of the polymer concentration ranges (0.1−20 mg/mL) studied, it was observed that the Guinier method gave a size distribution of molecules with the lowest- order-of-error fit. Partial Zimm and Berry plots methods of fitting gave errors that were larger than their corresponding $R_g$ values (at polymer concentrations less than 4 mg/mL), thus rendering values obtained from both data sets meaningless. These results indicate that at small *q* ranges, we have good agreement with Guinier analysis, and poor agreement with the other methods. The large uncertainty or magnitude in error (i.e., 39.4 ± 4.1 nm) observed at a low polymer concentrations of 0.1 mg/mL for the Guinier plot was due to the scattering intensity at this concentration which was barely above the scattering intensity of the solvent. Thus, high error would be introduced at this low concentration.

Light scattering studies on the average size of *m*-PBI as a function of increasing polymer concentration at fixed amounts of salt showed an initial collapse of the polymer chains in the polymer concentration regime of 0.1 to 4 mg/mL (Figure 4). This initial collapse has been observed for polyelectrolytes such as single (flexible) and double-stranded DNA (semiflexible) as well as for many synthetic polymers.[31,32] The initial collapse of the polymer chains in DMAc/4% LiCl can be attributed to the polymer molecules trying to minimize polymer−solvent interactions due to the poor DMAc/4% LiCl solvent mixture,[6] thus forming compact chains. We observed subsequent fluctuations in size without a significant decrease in the average size of the chains at increasing polymer concentration in the range of 4 to 10 mg/mL. However, at polymer concentrations greater than 9 mg/mL the average size of the polymer chains remained relatively constant at 31.2 ± 1.7 nm.

It has been shown that individual polymer chain conformation depends on the properties of their environment, i.e., the solvent.[33−35] Isolated polymer chains in the presence of a poor solvent tend to collapse toward compact states in which polymer−solvent contacts are minimized.[36] Kratky plot analysis showed that at very dilute polymer concentrations (less than 0.6 mg/mL), the polymer chain conformation was a random coil. However, at polymer concentration between 0.6 and 4 mg/mL, there was a change in the conformation to a wormlike chain while at concentrations between 4 and 20 mg/mL the polymer chain became “extended wormlike.”

From the analysis of the Kratky plots at increasing polymer concentrations (Figure 5), we observed a conformational transition from a flexible/random coil to an “extended wormlike” chain with an intermediate conformational transition to a wormlike chain. In this study, we referred to a wormlike chain as a chain possessing both flexible/random coil and “extended wormlike” structures, while an “extended wormlike” chain denoted a chain conformation that is almost rodlike in structure. The conformational transition from a flexible to a wormlike chain can be related to the collapse of the polymer chain. It has been observed that stiff polymer chains with strong intrachain interactions collapse into conformations of toroids or rodlike structures with long-range order.[37−39] Similar size and shape changes were also observed as a function of increasing salt concentrations at fixed polymer concentrations (Figure 6). However, at low salt concentrations (less than 3% LiCl), the chain conformation was wormlike as opposed to the random coil that was observed when polymer concentration was low (Figure 7). This slight deviation in polymer conformation at low salt concentrations could be an indication that varying polymer concentration has a more pronounced effect on the chain conformation than varying the salt concentration.

Circular dichroism studies indicated the presence of optical activity at polymer concentrations above 2 mg/mL for *m*-PBI (Figure 8). Optical activity was observed by noticing changes in the peak regime of wavelength range (280−390 nm), with PBI absorbance occurring at ∼ 350 nm. At concentrations less than 4 mg/mL, no defined structure (i.e., no optical activity) was observed, due mainly to the formation of both flexible/random coil and wormlike chains in this concentration range, as observed using light scattering measurements. The presence of optical activity at concentrations in the range of 4.0 to 25.0 mg/mL supports our light scattering findings of a conformational

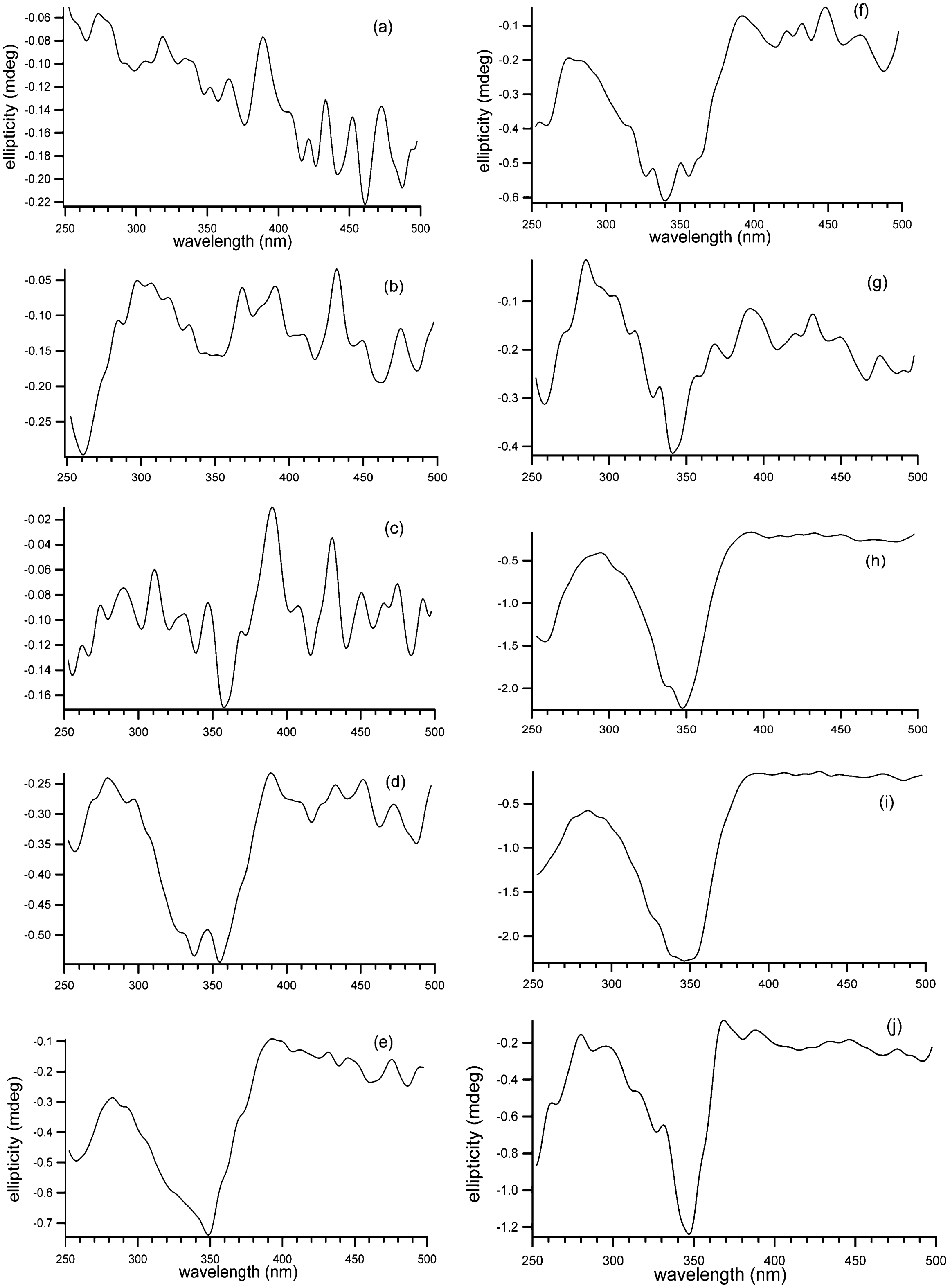

**Figure 8.** CD spectra of *m*-PBI/DMAc/4% LiCl solutions at varying polymer concentrations (mg/mL): (a) 0.4; (b) 1.0; (c) 2.0; (d) 4.0; (e) 6.0; (f) 9.0; (g) 13.0; (h) 17.0; (i) 20.0; (j) 25.0.

transition to "extended wormlike" chains formed in this polymer concentration range. Our circular dichroism measurements indicated that as polymer concentration was increased from 0.4 to 25.0 mg/mL, there was a conformational transition of the polybenzimidazole chains from a random coil to a helix. Earlier results using proton NMR spectroscopy[40] to monitor proton chemical shifts have indicated conformational changes for PBI in DMAc/LiCl solutions. Similar conformational transitions from a random coil to a helix has been shown to occur in the polysaccharide family of carrageenans which are anionic polyelectrolytes. This has been reported for *κ*-carrageenan, and was dependent on polymer concentration, solvent, temperature, pH, type of ions, and presence of a denaturing agent.[41,42]

Both positive and negative birefringence was observed for *m*-PBI in the polymer concentration regime studied (0.4−30 mg/mL) (Figure 9). The presence of either one depends on the

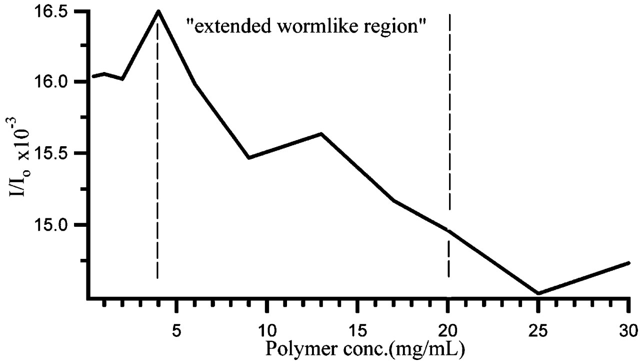

**Figure 9.** Dependence of birefringence, $I/I_o$ , on increasing polymer concentration at fixed salt (4% LiCl).

optical anisotropy of the polymer chain segments. At concentrations less than 4 mg/mL, both the flexible and wormlike polymer chains exhibited no noticeable birefringence. However at a polymer concentration of 4 mg/mL, positive birefringence was observed, confirming the formation of structure as was previously determined from light scattering and circular dichroism measurements at this concentration. An unusual decrease in birefringence was observed at increasing concentrations (6−25 mg/mL). This decrease in birefringence was contrary to that observed at 4 mg/mL. This unusual decrease in birefringence could be the result of relaxation due to the degree of flexibility of the chains as well as to deformation of the polymer chains due to the influence of the laser's intensity.[43] A transient electric birefringence experiment on wormlike macromolecules under the influence of an electric field of arbitrary strength has been shown in computer simulation studies to lead to deformation of the molecules, which results in a decay of their birefringence profiles over time.[43] A positive birefringence observed at a very high concentration of 30 mg/mL could be an indication of the formation of both complex and associating structures due to the aggregation of the molecules in this high concentration regime. The associative behavior of PBI chains in solutions of higher concentrations observed in this study may influence the variation in the morphology (gel structure) of sol−gel membranes for fuel cell applications. The variations in the gel structures could be due to the different stacking arrangements of helixes formed at moderate to high polymer concentrations which are usually employed in the preparation of polybenzimidazole membranes via a polyphosphoric acid sol−gel process.

## Conclusions

Static light scattering has been used for the first time to obtain the molecular parameters ($M_w$, $R_g$, and $A_2$) as well as to study the chain conformation of a high molecular weight semiflexible meta-polybenzimidazole in DMAc/4 % LiCl. Molecular parameters obtained from Zimm plot measurements are in good agreement with the previously measured inherent viscosity of the samples. Reduced viscosity measurements indicated that the polymer behaved like a polyelectrolyte in solution thus accounting for the observed conformational transitions at increasing polymer concentrations. Size distribution of *m*-PBI molecules in solution obtained from Guinier analysis at small $q$ region showed that these molecules are mid-size particles (∼20−50 nm).

Light scattering studies indicated that a conformational transition from a random coil to an "extended wormlike" chain occurred in *m*-PBI when polymer concentration was increased (0.1−20 mg/mL). An intermediate conformational transition from a random coil to a wormlike chain was observed by light scattering (between 0.1 and 4 mg/mL) and viscosity measurements (0.1−1.8 mg/mL). Circular dichroism measurements indicated the occurrence of conformational transitions from a random coil to a helix when polymer concentration was increased as well as the presence of optical activity at concentrations above 2 mg/mL. Birefringence measurement of *m*-PBI molecules indicated the influence of the laser's intensity in inducing relaxation, as well as deformation, on the polymer chains at concentrations between 6 and 25 mg/mL.

A combination of viscosity and static light scattering techniques has proven to be a powerful tool in studying the solution behavior of *m*-PBI in DMAc/4% LiCl solutions. For instance, from reduced viscosity measurements, it was observed that a conformational transition from a random coil to a compact chain occurred at increasing polymer concentrations (0.1−1.8 mg/mL). Similar conformational transitions were observed using light scattering techniques at polymer concentrations between 0.1 and 2 mg/mL. However, at concentrations of 4 mg/mL and above, the polymer chain became "extended wormlike". These conformational changes from a random coil to an "extended wormlike" chain in solution could occur prior to gel formation (at high polymer concentrations) for polybenzimidazole membranes prepared via a sol−gel process.

In summary, our results indicated that the polymer chains of *m*-PBI collapsed with increasing polymer concentration (at fixed LiCl content) to form compact and complex helical structures. These helical structures, which were formed at polymer concentrations above 2 mg/mL, experienced subsequent contraction and expansion thus accounting for the fluctuations in chain size observed within concentration ranges of 4 to 10 mg/mL. As concentrations increased further from 10 to 20 mg/mL, the polymer chain "stretched," thus accounting for the relatively constant size observed. At higher concentrations such as 30 mg/mL, there is a possible formation of both complex and associating helical structures as indicated by the positive birefringence observed at the concentration.

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