Aggregation Behavior of Polybenzimidazole in Aprotic Polar Solvent

ARTICLE *in* MACROMOLECULES · MARCH 2007

Impact Factor: 5.8 · DOI: 10.1021/ma070049q

4 AUTHORS, INCLUDING:

Arindam Sannigrahi
Pidilite Industries Ltd
17 PUBLICATIONS **331** CITATIONS
SEE PROFILE

Arunbabu Dhamodaran
McGill University
13 PUBLICATIONS **267** CITATIONS
SEE PROFILE

Murali Sankar Rajavelu
Central Leather Research Institute
19 PUBLICATIONS **184** CITATIONS
SEE PROFILE

Aggregation Behavior of Polybenzimidazole in Aprotic Polar Solvent

Arindam Sannigrahi, Dhamodaran Arunbabu, R. Murali Sankar, and Tushar Jana*

School of Chemistry, University of Hyderabad, Hyderabad, India

Received January 8, 2007; Revised Manuscript Received February 12, 2007

ABSTRACT: We report a study of aggregation behavior of polybenzimidazole (PBI) in polar aprotic solvents such as dimethylacetamide (DMAc). The photophysical studies of the PBI solution at various concentrations show concentration quenching and reveal that aggregated structures are formed when the polymer concentration is increased. The decay profiles obtained from time-resolved fluorescence study for low (0.00154 g/dL) and high (0.154 g/dL) concentrations of PBI in DMAc solution fit into a triexponential decay, surprisingly high concentration shows a growth (negative pre-exponential factor) in the decay profile, providing a support for excimer formation. The excited-state life time for the aggregated/excimer structure is found to be 4.14 ns, longer than that for the free polymer chains for which the life time is 502 ps. The concentration dependence emission spectra attribute that the aggregation/excimer formation is an intermolecular process. An abrupt decrease of Huggins constant and reduced viscosity with increase in concentration indicate the conformational transition of polymer chains of PBI from compact coil to an extended helical rodlike structure. The NMR and viscosity studies demonstrate that the intra- and intermolecular interactions (interchain hydrogen bonding) play an important role for the conformational transition and aggregation process. Transmission electron microscope images support the conclusion drawn from other studies; show helical rods for high concentration and featureless morphology for low concentration. The circular dichroism spectrum is also in agreement with the helical characteristics of aggregated structure. The temperature-dependent NMR and viscosity studies show that the disruption of interchain hydrogen bonding with increasing temperature destabilizes the aggregated structure at higher temperature.

Introduction

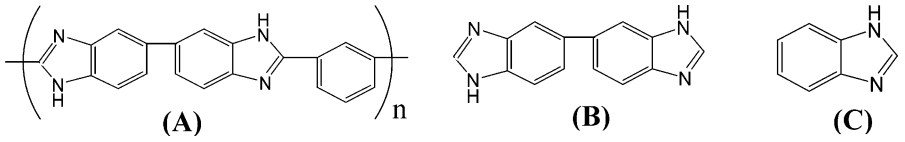
Polymers and biopolymers are known to form variety of aggregated structures in solution. These macromolecules in solution often interact with each other through the intermolecular interaction resulting in ordered structures. Intramolecular interactions are also possible when different parts of single chain interact with each other. The major driving forces for both inter and intramolecular interactions are mainly hydrogen bonding, electrostatic interactions, and hydrophobic interactions etc.[1,2] The outcomes of these interactions are very fascinating; it is possible to tune various molecular properties of the macromolecules by controlling the nature and extent of these interactions. It has been shown that for biopolymers such as peptides, proteins etc. both intra- and intermolecular interactions play an important role in many biological functions.[3−5] A thorough investigation of the mechanism and the factors influencing these interactions on synthetic polymers is very much desirable since these synthetic polymers serve as model systems for biopolymers. A large number of efforts have been already put forward to address these issues in the literature.[3,4,6−8] The effect of intra- and intermolecular interactions on the polymer chain conformation, conformational transition have been demonstrated extensively for polyelectrolyte−surfactant complexes in solutions.[9] The majority of the research reports have been focused mainly on vinyl polymers, polypeptides and simple structure polymers.[3−9] There are few reports available in the literature addressing these interactions for polymers with highly complex molecular structures.[10−12] For example, polymers having aromatic structure in the main chain and heteroatoms in the chain and also many condensation polymers have not been studied thoroughly to look at their aggregation behavior in different solvents manifested by intra- and intermolecular interactions.

* To whom correspondence should be addressed. Telephone: (91) 40 23134808. Fax: (91) 40 23012460. E-mail: tjsc@uohyd.ernet.in.

Polybenzimidazole (PBI, Scheme 1) is an aromatic heterocyclic thermally stable polymer that possesses both proton donor (−NH−) and proton acceptor (−N═) hydrogen-bonding sites, which exhibit specific interactions with protic and aprotic polar solvents.[12,13] The availability of hydrogen-bonding sites in the polymer chain made it a suitable candidate for miscible blending with various polymers possessing carbonyl and sulfonyl functionality.[14,15] For example PBI forms a miscible blend in a wider composition range with polyimide, poly(ether imide), and sulfonated poly sulfone through the specific interaction of its proton donating (−NH−) site with the proton accepting site of the other polymers.[14,15] PBI is being used for various applications, in particular, for high temperature applications, fiber spinning, and reverse osmosis membranes, because of its excellent thermal−chemical tolerance and film forming capability.[16] Recently, phosphoric acid (PA) doped PBI membrane was found to be the most promising material to use as polymer electrolyte in high-temperature proton exchange membrane fuel cell (PEMFC).[17] It has been shown that the PA-doped PBI exhibits high proton conduction at high temperature up to 200 °C, excellent oxidative and thermal stability, low gas permeability, and nearly zero water drag coefficient.[17−19] A variety of approaches have been explored to prepare PA doped PBI membrane. Most of these approaches deal with the dissolution of the solid polymer in polar aprotic solvent such as dimethylacetamide (DMAc) and then fabrication of membrane followed by soaking in polar protic solvent such as phosphoric acid (PA).[17−20] Recently, Xiao et. al made PA-doped PBI membrane via sol−gel process by direct casting of high molecular weight PBI polymerization solution in polyphosphoric acid (PPA), and subsequently, PPA is hydrolyzed to PA.[21,22] It was also shown that the imidazole nitrogens present in the polymer backbone play a crucial role for the doping process through a specific interaction with the solvent molecule. In a recent article, we have demonstrated that the fairly concentrate

10.1021/ma070049q CCC: $37.00
Published on Web 03/13/2007

Scheme 1. (A) Poly(2,2′-(*m*-phenylene)-5,5′-bibenzimidazole) (PBI), (B) 3,3′-Bibenzimidazole (BBI), and (C) Benzimidazole (BI)



solution of PBI in PA produces a thermoreversible polymer gel.[23] The driving force for the gel formation is the hydrogen bonding of the PA molecules with the nitrogen atoms of imidazole ring, producing the PBI crystallites.[23] We were able to show that a conformational transition of PBI chain takes place when a hot PBI solution in PA cools down to gelation temperature.[23] In the present article, we demonstrate the possible aggregation behavior of a very dilute PBI solution in polar aprotic solvent such as DMAc, which may reveal a better understanding of the polymer chain conformation in dilute solution and help us to get an idea of preparing membrane of superior quality from both polar protic and polar aprotic solvents.

Fluorescence spectroscopy has been utilized as a prime tool for the investigation of intra- and intermolecular interactions of polymer chains and their aggregations.[7,10−12,24−27] The photophysical studies of polymer solution have been limited almost entirely to olifinic polymers with aromatic[24] and heterocyclic pendent groups such as polystyrene,[25] poly(*N*-vinyl carbazole),[26] poly(vinyl anthracene)[27] etc., and their copolymers.[28] All these polymers show either intra- or intermolecular[28] excimer formation in solution. Exciplex formation in polymers was also studied as a measure of molecular interactions.[10] The fluorescence studies of condensation polymers[10,29] especially aromatic heterocyclic polymers such as polybenzimidazole,[11,30] polyquinoline,[12] etc. were attempted to elucidate intra- and intermolecular aggregations. However these studies are not as extensive as olifinic polymers; perhaps the poor solubility of these aromatic heterocyclic polymers in most common organic solvents is the major restriction for photophysical studies in solution. Huang et al. reported that polyquinolines form excimers in acidic solution resulting in concentration quenching and showed that excimer formation is controlled by intermolecular repulsion between the polymer chains.[12] Kojima showed that the molecular aggregation in the ground state of PBI in DMAc solution is due to the overlapping of polymer coils.[11] It is to be noted that the PBI used by Kojima[11] which has 4, 4′ -oxybibenzyl linkage with imidazole group is not exactly similar to Scheme 1 where *m*-phenylene linkage is present. However, in the literature there is no thorough investigation of various photophysical processes of PBI (Scheme 1) using both steady state and time-resolved fluorescence study at various concentration. This could probably give us a better understanding of intra- and intermolecular interaction of the polymers in solution, which leads to aggregation/excimer formation.

In this article, we report intra- and intermolecular interaction of dilute PBI in DMAc solution studying steady state and time-resolved fluorescence, viscosity at different temperatures, nuclear magnetic resonance at different temperatures and different concentrations, and morphology obtained from transmission electron microscopy.

Experimental Section

Materials. 3,3′,4,4′-Tetraaminobiphenyl (TAB) and polyphosphoric acid (115%) were purchased from Sigma-Aldrich. Isophthalic acid (IPA) was received from SRL, India. Benzimidazole (BI) and sulfuric acid (98%) were received from Merck, India. Dimethylacetamide (HPLC grade) and deuterated dimethyl sulfoxide (DMSO-d_6) were received from Qualigens (India) and Merck (India), respectively. All chemicals were used as received.

PBI Synthesis. Equal moles of TAB and IPA were taken into a three neck flask with PPA and the reaction mixture was stirred continuously in nitrogen atmosphere at 190−210 °C for ∼24 h. The PBI polymer was isolated, neutralized with sodium carbonate, washed thoroughly with water, and dried in a vacuum oven at 100 °C for 24 h. The dried polymer was characterized by viscosity measurements in H_2SO_4 (98%) and has an inherent viscosity (IV) value of 0.62 dL/g at 30 °C.

3,3′-Bibenzimidazole (BBI) Synthesis. BBI (Scheme 1) synthesis was carried out according to the previously reported method[31] and characterized using NMR, IR, and LC−MS.

Viscosity. The viscosity measurements of PBI solutions in DMAc were carried out at various temperatures (308−343 K) using a Cannon Ubbelohde capillary dilution viscometer (model F725). The viscosity data were analyzed according to the Huggins equation

$$\frac{(t - t_0)}{C} = \frac{\eta_{sp}}{C} = \eta_{red} = [\eta] + k[\eta]^2 C \qquad (1)$$

where t and t_0 are the flow time of the polymer solution and solvent, respectively, C is the concentration of polymer in g/dL, η_{sp}, η_{red}, and $[\eta]$ are the specific, reduced, and intrinsic viscosities of the polymer solution, respectively, and k is the Huggins constant.

Spectroscopy. Electronic absorption spectra were recorded on a Shimadzu model UV-3100 UV−visible spectrometer. Steady-state fluorescence emission spectra were recorded on a Jobin Yvon Horiba spectrofluorimeter (model Fluoromax-3). Time-resolved fluorescence measurements were carried out using a time-correlated single-photon counting (TCSPC) spectrophotometer (IBH Nano LED). A diode laser (λ_{exc} = 374 nm) was used as the excitation source and the instrument response time was 75 ps (fwhm). The emission was detected at right angle to the excitation beam using a Hamamatsu 323P MCP photomultiplier. A dilute solution of Ludox in water was used to record the lamp profile. The decay curves were analyzed by nonlinear least-squares iteration using IBH DAS6 (Version 2.2) decay analysis software. All NMR spectra of PBI solutions in DMSO-d_6 at various dilution and temperatures were recorded using a Bruker AV 400 MHz NMR spectrometer. Circular dichroism (CD) spectra of polymer solutions were recorded on a spectropolarimeter (Jasco-810) at 30 °C using a 2 mm quartz cuvette.

Microscopy. The morphological features of the PBI samples obtained from various solution concentrations were examined using a Jeol (JEM 2000) transmission electron microscope (TEM) operating at 120 kV. For TEM experiments, appropriate concentrated polymer solutions were dropped in carbon coated copper mesh and imaged.

Results and Discussion

Spectroscopy. The absorption spectra of PBI and nonpolymeric model compounds such as BBI and benzimidazole (BI) (Scheme 1) in DMAc are presented in Figure 1. The PBI concentration is expressed by considering one repeat unit as 1 mol PBI. The lower wavelength peaks; 344 nm for PBI,[32] 295 nm for BBI, and 270 nm for BI are due to $\Pi \rightarrow \Pi^*$ transition of the imidazole moiety and longer wavelength peaks; 440 nm for PBI (inset of Figure 1), 350 nm for BBI and 345 nm for BI are due to $n \rightarrow \Pi^*$ transition of the imidazole ring. The large bathochromic shift of the $\Pi \rightarrow \Pi^*$ absorption maxima for PBI and BBI is due to increased conjugation between phenylene groups and imidazole rings. A more distinct red shift of the polymer peaks compared to those nonpolymeric model compounds is attributed due to the large extent of

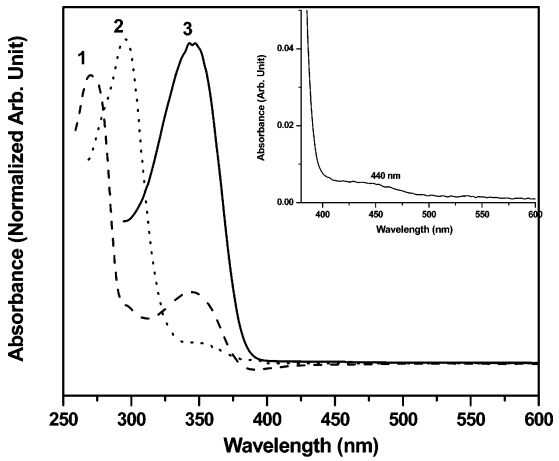


Figure 1. Absorption spectra of (1) BI, (2) BBI, and (3) PBI in DMAc solution as recorded with a cuvette of 1 cm path length. Concentrations are (1) 5.9×10^{-4}, (2) 1.17×10^{-3}, and (3) 1.54×10^{-3} g/dL (all are 5×10^{-5} M concentration). Inset: Magnified spectra of PBI to show the 440 nm peak position.

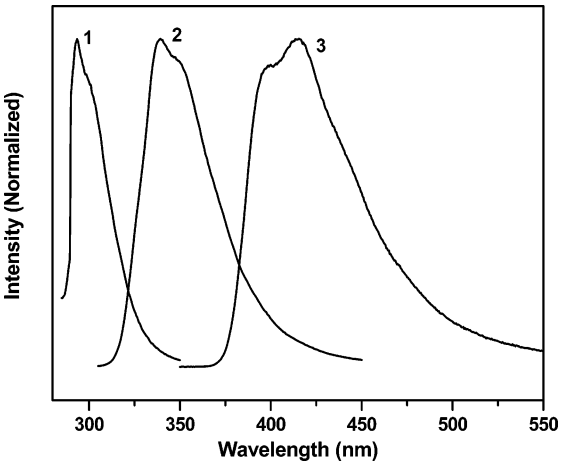


Figure 2. Fluorescence emission spectra of (1) BI, (2) BBI, and (3) PBI in DMAc solution. Concentrations are identical to Figure 1. Excitation wavelength (λ_{exc}): (1) 275, (2) 295, and (3) 340 nm.

conjugation along the polymer chain. The inset of Figure 1 shows that PBI has a very long tail toward longer wavelength which becomes prominent as the concentration of the solution increases (Supplementary Figure 1). In contrast to PBI, we have not observed any such long tail for nonpolymeric model compounds. This observation indicates the possibility of aggregation of polymer chains through overlapping of polymer coils at higher concentration.

The major fluorescence emission of polybenzimidazole and molecules with imidazole moiety has been assigned previously by several authors as the emission from the excited ^1L_b state.[11,33] The emission spectra of PBI, BBI, and BI in DMAc of similar concentrations are shown in Figure 2. The emission spectrum of PBI shows two fluorescence bands at 398 and 416 nm. These peaks are assigned to the 0−0 and 0−1 transitions from the excited ^1L_b state in the benzimidazole ring of PBI.[11] The spectral nature and shapes presented in Figure 2 are consistent with the earlier report of very similar molecules by Kojima.[11] The emission bands for PBI are observed at longer wavelength relative to those nonpolymeric molecules is the result of existence of higher conjugation in the polymer.[11] Figure 3, supplementary Figure 2 show the emission spectra of PBI and BBI, respectively, at various concentrations in DMAc. In all the cases emission intensity is decreased with increasing solution concentration indicating the presence of concentration quenching. The peak at 398 nm of PBI gradually diminishes with increasing PBI concentration and finally at higher concentration (0.154 g/dL) 416 nm peak exists along with another broad peak at ∼548 nm. The concentration dependence of emission intensity for PBI is almost similar to nonpolymeric molecules; though it is more distinctly visible for PBI. The ratio of the peak intensities (longer wavelength peak to lower wavelength peak) in the emission spectra increases with concentration. The presence of concentration quenching and enormous increase of peak intensity ratio with concentration indicate that the polymer chains are aggregated among themselves intermolecularlly at higher concentration. Earlier Kojima calculated the critical quenching volume for a similar type of PBI polymer and showed that intermolecular aggregation of polymer chains takes place in DMAc.[11]

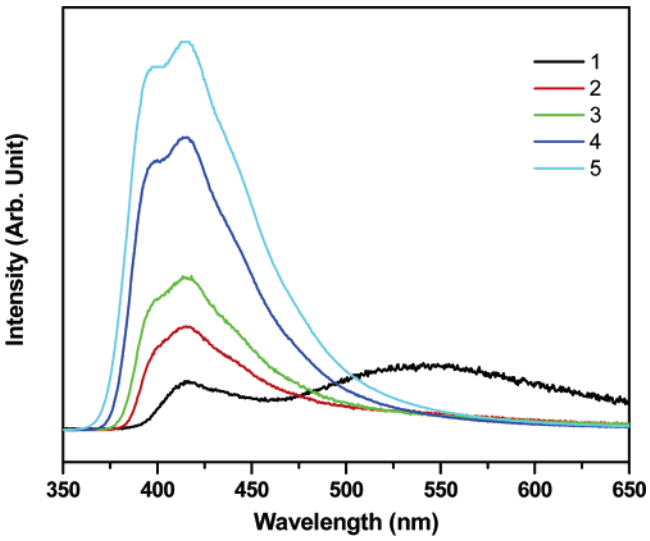


Figure 3. Fluorescence emission spectra of PBI in DMAc solution at various concentrations; (1) 1.54×10^{-1}, (2) 1.54×10^{-2}, (3) 5.0×10^{-3}, (4) 1.54×10^{-3}, and (5) 1.54×10^{-4} g/dL. Excitation wavelength (λ_{exc}) is 340 nm.

Moreover, Figure 3 shows a broad emission band at longer wavelength (∼548 nm) for the highly concentrated (0.154 g/dL) solution. For similar solution concentrations, Kojima[11] have not observed this broad fluorescence band. We have not observed this broad emission peak for nonpolymeric molecules at similar concentration. To understand the role of this broad peak, we have recorded the emission spectra of a series of PBI solutions where the concentration gradually increases, and this is presented in Figure 4. From Figure 4, it is clearly visible that as concentration increases the broad 548 nm peak becomes prominent and the intensity of 416 nm band decreases. It is worth noting that Figure 4 shows an isoemissive point at ∼460 nm. The presence of a broad emission at a higher wavelength and isoemissive point attributes the formation of a complex between excited-state and ground state molecules, known as the excimer complex.[34] Olifinic polymers with pendent aromatic groups very often form an excimer both in solution and in the solid state.[24,25,28] Though it is very rare for a polymeric system such as the present one, our steady-state fluorescence study on PBI at various concentrations (Figure 4) clearly satisfies the required criteria for excimer formation. It is also important to note that the nonpolymeric molecules such as BBI and BI do not show a similar photophysical behavior at similar concentrations. Hence the spectral behavior presented in Figure 4 is exclusively for a polymeric system in DMAc at higher concentration. Hence, we can argue that PBI in DMAc forms an excimer; the broad 548 nm peak is for excimer

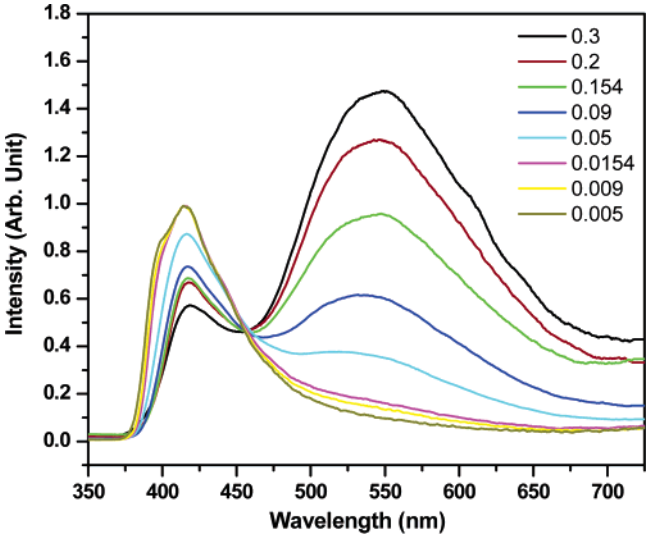


Figure 4. Fluorescence emission spectra of PBI in DMAc solution at indicated concentrations (in g/dL); Excitation wavelength (λ_{exc}) is 340 nm.

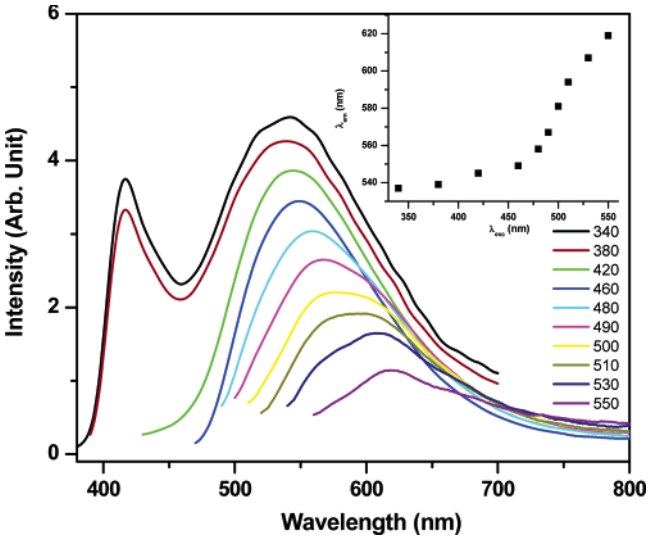


Figure 5. Dependence of fluorescence emission spectra on excitation wavelength (indicated in the figure) for PBI in DMAc solution (concentration is 0.2 g/dL). Inset: plot of λ_{em} against λ_{exc}.

emission and the 416 nm peak is for monomer emission. The excimer and monomer emission intensities are denoted as I_E and I_M, respectively. However, the question arises that the broad 548 nm peak is really the emission from an excited-state species (excimer) or an aggregated species which forms in the ground state itself and emits separately at longer wavelength. To clarify this, we have adopted two methods; first we have recorded emission spectra of a concentrated (0.154 g/dL) solution by varying the excitation wavelength, and second, we have carried out a time-resolved fluorescence life time measurement of PBI in DMAc solution at very dilute (0.00154 g/dL) and high (0.154 g/dL) concentrations. If emission spectra depend on excitation wavelength, then aggregation in the ground state occurs,[11,35] and if a growth is observed (a negative pre-exponential factor) in the decay profile, then excimer formation is attributed.[36] Figure 5 shows excitation wavelength (λ_{exc}) dependence emission spectra for a concentrated solution. As the λ_{exc} increases, the 548 nm peak shifts toward the longer wavelength side. Similar observations were reported for PBI and imidazolium-based room-temperature ionic liquids; this is explained as molecular aggregation in the ground state.[11,35] The dependence of the emission band on λ_{exc} can be explained with the help of absorption spectra presented in Figure 1 and Supplementary Figure 1. A long tail in the absorption band indicates the presence of a large number of aggregated species in the ground state that are energetically different. Each aggregated species is characterized by its own absorption and fluorescence maxima. When the λ_{exc} is shifted, a different species is excited and emission characteristic of that species is observed. Therefore, we can conclude that molecular aggregation is present in the PBI in DMAc solution. The extent of emission peak position shift is shown in the inset of Figure 5.

The decay profiles of dilute (0.00154 g/dL) and concentrate (0.154 g/dL) PBI in DMAc solution are obtained by exciting the samples at 374 nm and monitoring the fluorescence at 417 nm. The decay profiles are shown in Figure 6, and the best fit and fluorescence decay parameters are presented in Table 1. The decay profiles for both the cases are found to follow a triexponential decay function as observed from Table 1. The nature of the decay profiles are not the same in both the cases. From Figure 6B, it is visible that for concentrate solution the decay profile shows a growth (a negative pre-exponential factor) which is not observed for dilute solution (Figure 6A). This observation is more understandable from Table 1; a negative fraction contribution (α_3) is obtained from concentrate solution. The growth in the decay profile and the negative pre-exponential are concrete proof for excimer formation.[36] Therefore, we can conclude that at higher concentration of PBI in DMAc excimer is formed and the broad peak at 548 nm is due to the excimer formation. Hence, from the above analysis it can be concluded that PBI forms aggregated species as well as exited state dimer (excimer) in the DMAc solution when the concentration of the solution is reasonably large. The broad 548 nm peak is the contribution from both aggregation and excimer. The excited-state life time for the concentrate solution is found to be 4.14 ns, longer than that for the dilute solution, for which the life time is 502 ps (Table 1). Previously, Liu et al.[37] showed that the excited-state life time depends upon the polymer chain conformations. Theoretically, they demonstrated that excited-state life time of polymer molecule becomes shorter as their root-mean square end-to-end distance decreases. Our results fit well with this reported argument. In the following sections, we have shown that as concentration of PBI in DMAc decreases the PBI chains form a compact coil structure and produce an extended conformation at higher concentration. Therefore, the excited-state life times of concentrate solution is longer (4.14 ns) than the dilute solution (502 ps). It is interesting to note that the ratio of aggregation or excimer intensity with monomer intensity (I_E/I_M or I_{548}/I_{416}) increases linearly with concentration (Figure 7). This indicates that the aggregation or excimer formation is an intermolecular process.[28,38] The large value of I_E/I_M for higher concentration attributes the presence of a strong intermolecular association in the aggregated species.

Viscosity. The interactions between polymer molecules and solvent have been studied previously by viscosity measurement method. The Huggins constant (k) and intrinsic viscosity ($[\eta]$) can be obtained for a dilute solution of a simple binary system using this method. It is well-known that the value of the Huggins constant (k) is used to predict the degree of the polymer−solvent interaction and can determine the polymer chain conformation in solution. The bigger value of k indicates that the polymer chains collapse and the intramolecular aggregation occurs easily. On the other hand, the smaller k value attributes extended conformations and the intermolecular interactions.[39,40] The viscosity of PBI at various dilutions was measured and a plot of reduced viscosity vs concentration is presented in

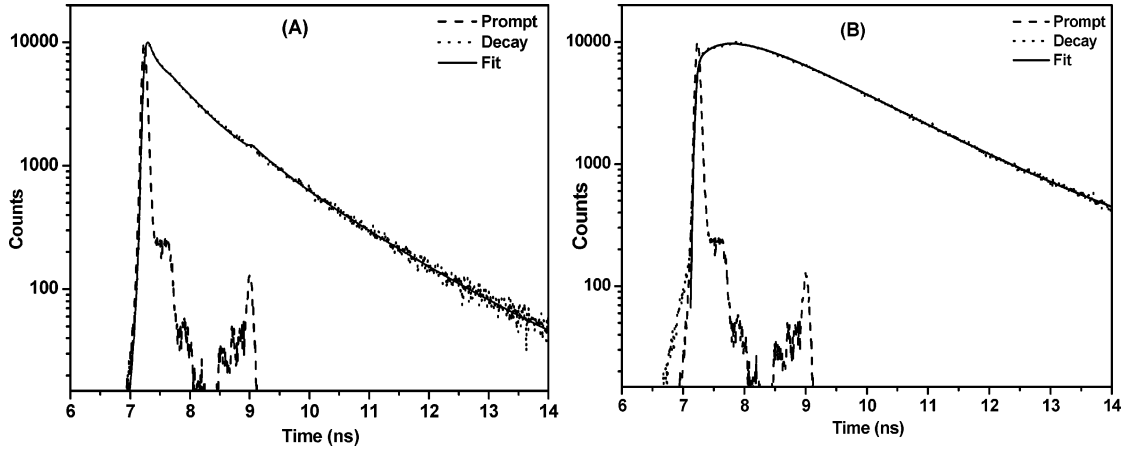


Figure 6. Time-resolved fluorescence decay profile of PBI in DMAc solution of two different concentrations: (A) 0.00154 and (B) 0.154 g/dL. $\lambda_{exc} = 375$ nm.

Table 1. Fluorescence Decay Parameters for PBI in DMAc Solutions at Different Concentrations[a]

PBI concn (g/dL)	τ_1 (ns)	α_1	τ_2 (ns)	α_2	τ_3 (ns)	α_3	τ_{av} (ns)	χ^2
0.001 54	0.59	0.35	1.5	0.17	0.07	0.48	0.502	1.27
0.154	1.56	3.13	6.31	0.07	0.55	−2.20	4.14	1.26

[a] The three lifetimes (τ_1, τ_2, and τ_3) and the respective fractional contributions (α_1, α_2, and α_3), the weighted average lifetime (τ_{av}), and the quality of fitting (χ^2) for the data in Figure 6 are shown.

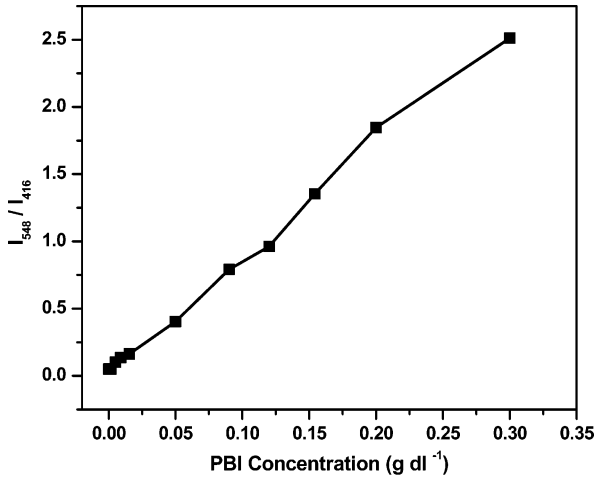


Figure 7. Dependence of excimer to monomer intensity ration with concentration of PBI in DMAc solution.

Figure 8. The Huggins constants (k) are estimated from the slopes of the viscosity vs concentration line. At the lower concentration region (0.075−0.009 g/dL) (Figure 8, curve b), the k value is 1.634; at the higher concentration region (0.6−0.1 g/dL) (Figure 8, curve a), it is 0.723. The higher k value (1.634) indicates the intramolecular interaction between different parts of the polymer chain, which results in a collapsed compact coil conformation of the polymer chain. At these concentrations, the excluded volume of polymer chain gets smaller and it does not allow the solvent molecules to go inside the polymer coil for swelling. As a result, polymer chains produce a compact coil structure. When concentration increases, more and more polymer molecules come into the solution and polymer chains start interacting with each other intermolecularly. Because of this intermolecular interaction, polymer chains swell by allowing solvent molecules to go inside the polymer coil, and the excluded volume of the polymer chain becomes larger. Therefore, it is reasonable to argue that the low k value (0.723) for

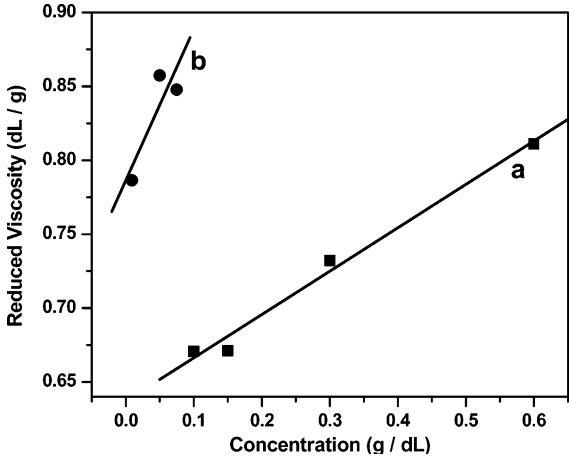


Figure 8. Concentration dependence of the reduced viscosity of PBI in DMAc solutions measured at 35 °C for two different concentrations regions: (a) 0.6−0.1 and (b) 0.075−0.009 g/dL.

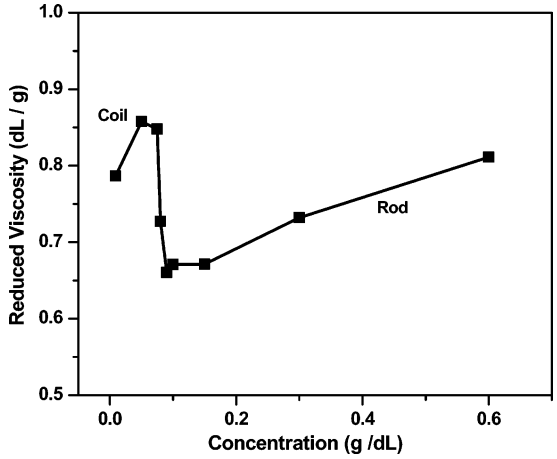


Figure 9. Plot of reduced viscosity against concentration of PBI in DMAc solutions measured at 35 °C.

the higher concentration range is in agreement with the above justification (intermolecular interactions), which results an extended conformation. Hence, at this concentration range, we would expect an extended rodlike aggregated structure. The above observations clearly exhibit a conformational transition of the PBI chains in DMAc solution when the solution concentration varies.[13] Figure 9 is the plot of reduced viscosity vs concentration for both the concentration region (similar to Figure 8) including the intermediate concentrations. The plot

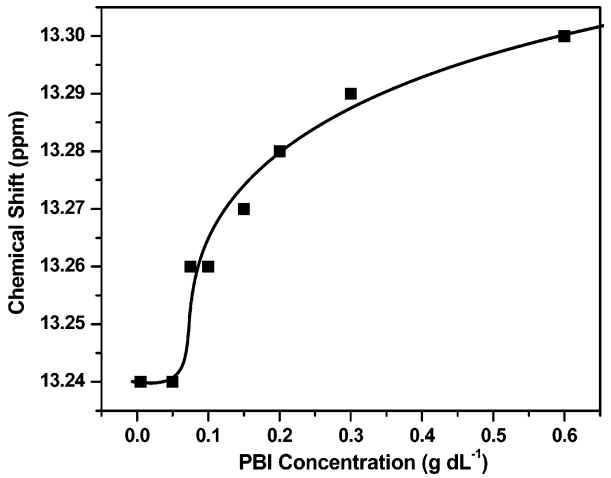


Figure 10. Dependence of imino proton signal with PBI concentration in DMSO-d_6 solution.

shows a clear transition of reduced viscosity and reveals that a conformational transition (compact coil to extended rodlike) in the polymer chain takes place.[9] Here, we can argue that in the smaller concentration range DMAc acts as a poor solvent (large *k* value and compact conformation) for PBI whereas it acts as a good solvent (small *k* value and extended conformation) in the higher concentration range. Therefore, from spectroscopic and viscometric studies, it is proven that upon increasing the PBI concentration in DMAc solution intramolecular interactions diminish but intermolecular interactions are enhanced, which triggers a conformation transition of polymer chain and produces an aggregated rodlike structure at higher concentration. A more detail understandings of the aggregation process with proofs are obtained from NMR and microscopic studies described in the preceding sections.

NMR Study. The concentration dependence proton NMR study can be utilized effectively to monitor the intermolecular interactions (interchain hydrogen bonding) between the polymer chains in solution. It has been shown that proton NMR spectroscopy is an effective tool for studying the conformational transition which arises by the disruption of interchain hydrogen bonding of polyelectrolyte−surfactant complexes in solution.[9] Unlike all other studies, NMR studies were carried out in DMSO-d_6 solvent, since it is less expensive compared to DMAc-d_9. PBI exhibits similar behavior in both the solvents. A representative proton NMR spectrum of PBI in DMSO-d_6 is presented in Supplementary Figure 3. The spectrum is consistent with the earlier reports. The peak at 13.3 ppm is due to the imino proton signal of imidazole rings and other peaks (7.65−9.15 ppm) are due to aromatic protons signals.[32, 41] The imino proton signal of PBI in DMSO-d_6 is gradually shifted upfield with decreasing concentration of the solution (Figure 10), which proves the disruption of intermolecular interactions such as hydrogen bonding[9] and formation of a more compact conformation of the polymer chain. This observation clearly indicates a conformational transition of the polymer chain from extended conformer to compact coil conformer. Hence, concentration dependence NMR spectroscopy is also consistent with our results discussed in the previous section. A more interesting result is obtained when we added 1% (w/v) urea in the PBI solutions, measured their viscosity and recorded NMR spectra. Urea is capable of breaking the hydrogen bonding. After addition of 1% urea in the 0.6 g/dL PBI solution, the 13. 3 ppm peak is shifted (upfield) and peak intensity is diminished (supplementary Figure 4) which indicates the breaking of interchain hydrogen bonding. Similar observations were reported before for PBI in DMAc/LiCl solution.[41,42] The intrinsic viscosity and Huggins constant obtained for the concentration range 0.6−0.1 g/dL at 35 °C in the presence of 1% urea are 0.3649 dL/g and 3.277, respectively. These values are remarkably different from the values obtained in the same concentration range at 35 °C in absence of urea (intrinsic viscosity 0.6369 dL/g and $k = 0.7233$). A decrease of the intrinsic viscosity and increase of the Huggins constant supports the decrease of intermolecular interactions or increase of intramolecular interactions.[8,39]

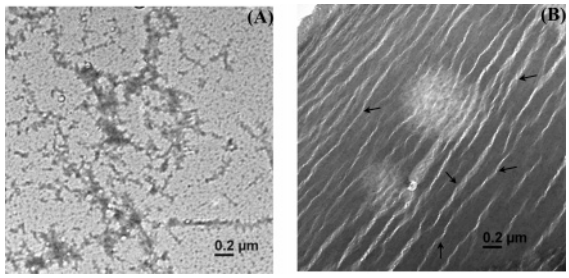


Figure 11. TEM micrographs of (A) 0.00154 and (B) 0.6 g/dL PBI in DMAc solution Arrows in the (B) image indicate the helical turns.

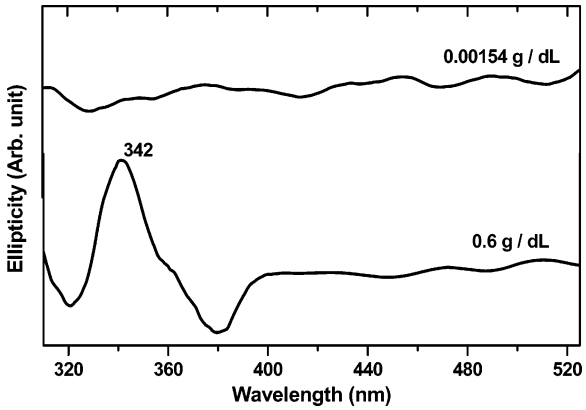


Figure 12. Circular dichroism spectra of PBI in DMAc solution at indicated concentrations.

Microscopy. It has been shown above that, at very low concentrations, the intramolecular interaction is prominent, which results in a compact coil type structure. Therefore, we do not expect any characteristic morphology at this concentration. Figure 11A represents the microscopic image obtained from a PBI solution in DMAc of concentration 0.00154 g/dL. The micrograph is almost featureless, except for a few polymer particles, consistent with our arguments from spectroscopic, viscometric and NMR data. We have demonstrated that with increasing concentration of PBI in DMAc, intermolecular interaction increases and produce an aggregated structure. Because of this aggregation process, the PBI chain in DMAc at higher concentration (0.6 g/dL) shows an extended rod conformation. Figure 11B represents the TEM image for PBI in DMAc solution of concentration 0.6 g/dL. The morphology of Figure 11B is entirely different compared to that of Figure 11A, which exhibits the effect of PBI concentration on morphology. From Figure 11B, it is seen that PBI forms an extended rod-type morphology. It is important to note that all the rods in the image show helical turns (indicated by arrows). The circular dichroism (CD) studies show the presence of optical activity of a 0.6 g/dL solution at 342 nm and the absence of any optical activity of dilute PBI solution (Figure 12). This observation exhibits the presence of an ordered structure for PBI at higher concentration whereas no such defined structure for PBI is evident at low concentration. Similar CD results were observed for PBI in DMAc/LiCl solution.[13] Hence these results

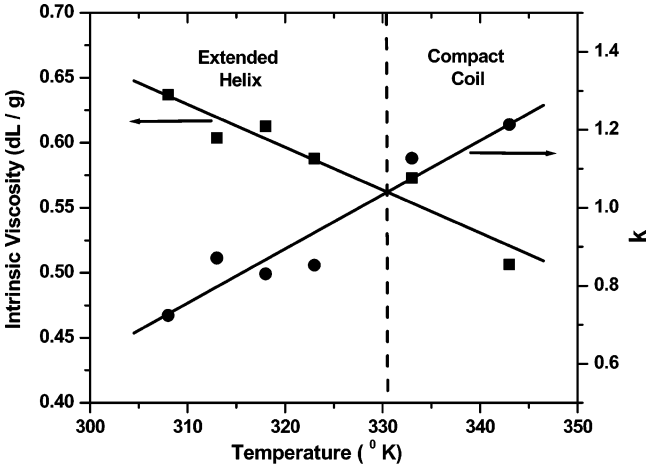


Figure 13. Effect of temperature on Huggins constant and intrinsic viscosity of PBI in DMAc solutions for the concentrations regions 0.6−0.1 g/dL.

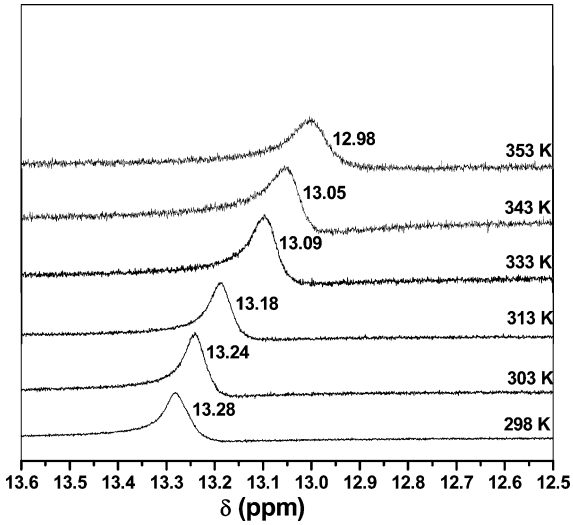


Figure 14. Temperature-dependent imino proton signals of PBI in DMSO-d_6. Concentration is 0.3 g/dL.

prove that a helical rodlike structure formation takes place when the solution concentration is high. Therefore, we can conclude that the microscopic and CD data also support a conformational transition (compact coil to extended helical rodlike) of PBI chains when the concentration of the polymer in solution increases.

Temperature Effect. We have observed from the above discussion that at the higher concentration (0.6−0.1 g/dL) of PBI in DMAc at room temperature, the polymer chains form an aggregated structure and exist as an extended helical conformation because of the intermolecular interaction (interchain hydrogen bonding) between themselves. This conclusion immediately brings up a question: How stable is this aggregated structure in response to the environmental stimuli such as temperature change? And answer to this question is of utmost importance to know since it could provide a valuable piece of data which may help us to prepare a good quality membrane for PEMFC applications. We have carried out temperature-dependent studies such as viscosity and NMR to answer the above question. Figure 13 shows the variation of viscosity parameters with temperature (308−343 °K). The intrinsic viscosity of PBI in DMAc decreases and Huggins constant increases as temperature increases (Figure 13). Kojima et al.[43] have also observed the decrease of intrinsic viscosity with increase in temperature. It is well-known that for a polymer of fixed molecular weight, intrinsic viscosity is directly proportional to the end to end distance of the polymer chain. The PBI used in this article has a fixed molecular weight (inherent viscosity 0.62 dL/g). So, the decrease of intrinsic viscosity with increase in temperature indicates the shrinkage of polymer chains; i.e., chains are collapsed at higher temperatures. Similarly, the increase of Huggins constant with increase in temperature attributes that at higher temperatures the solvent behaves as a poorer solvent for the polymer chains, producing a compact coil type conformation. The above results clearly demonstrate that at higher temperature, aggregated structure with extended helical polymer chain conformation does not exist. The probable reason behind this is that intermolecular interaction such as interchain hydrogen bonding breaks at higher temperature. A better understanding of the disruption of interchain hydrogen bonding is obtained from the temperature-dependent NMR studies of PBI solution. The imino proton signal of PBI (concentration is 0.3 g/dL) at various temperatures are presented in Figure 14. An upfield shift of the imino proton signal is observed with increase in temperature. The upfield shift of the imino proton, a strong hydrogen-bonding proton, is due to the disruption of interchain hydrogen bonding. Earlier we have shown the conformational transition of PBI chains in phosphoric acid solution with temperature.[23] Therefore, it can be argued that at higher temperature the aggregated structure of concentrated PBI solution breaks and a conformational transition occurs from extended helical conformer to collapsed compact coil conformer. Similar type of observation and conclusion was made by MacKnight et al. for polyelectrolyte−surfactant complexes in solution with an increase of trifluoroacetic acid (TFA) content in the solution.[9]

Conclusion

We have studied the aggregation behavior of PBI in polar aprotic solvent such as dimethylacetamide (DMAc) by varying the polymer concentration in the solution. Various methods such as photophysical, viscometric, microscopic, and NMR have been used to study the aggregation behavior and associated conformational transition of the polymer chains. Steady state and time-resolved fluorescence spectroscopy studies demonstrated the formation of an aggregated structure at higher concentration of PBI in solution. These photophysical studies also proved excited-state complex, i.e., excimer formation at higher concentrations. It has been also shown that both aggregation and excimer formation is an intermolecular process. Viscometric studies indicated that a conformational transition from a compact coil to an extended helical rodlike structure takes place in PBI solution when polymer concentration is high. A sharp decrease of Huggins constant and abrupt decrease of reduced viscosity with increase in polymer concentration validated the conformational transition argument. The intramolecular interaction within the various parts of polymer chain at lower concentrations and intermolecular interactions between the polymers chains at higher concentrations could be the probable reason behind the conformational transition. An additional evidence for conformational transition is obtained from the NMR studies. An upfield shift of the imino proton signal indicated the disruption of interchain hydrogen bonding. Microscopic images and CD spectra obtained from various polymer concentrations also supported the conformational change behavior of PBI in DMAc and helical rod shaped morphology for a 0.6 g/dL solution. Finally, temperature-dependent studies (viscosity and NMR) showed that the aggregated structure is not stable at higher temperature. Therefore, in summary, we can conclude that

polymer chains of PBI in DMAc solution form a coil structure at lower concentration due to intramolecular interaction and produce an aggregated extended helical rodlike structure at higher concentration because of intermolecular interaction, although the aggregated structure is not stable at higher temperature.

Acknowledgment. We gratefully acknowledge financial support by the DST (Fast Track Grant No. SR/FTP/CS-49/2005) and UPE programme of the UGC. We thank Prof. A. Samanta and Mr. A. Paul for helping us with the time-resolved experiment, analysis, and a helpful discussion. We also thank Dr. S. Malik of Kyushu University, Japan, for helping us with TEM experiments.

Supporting Information Available: Figures showing the absorption spectra of PBI in DMAc solution at various concentrations, fluorescence emission spectra of BBI in DMAc solution at various concentrations, proton NMR spectrum of PBI in DMSO-d_6, and upfield shift and reduced intensity of imino proton signal in the presence of urea. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Lehn, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 90.
(2) Lehn, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.
(3) Bekturov, E. V.; Bimendina, L. A. *Adv. Polym. Sci.* **1981**, *41*, 99.
(4) Tschuchida, E.; Abe, K. *Adv. Polym. Sci.* **1982**, *45*, 1.
(5) Whitesides, G.; Mathias, J.; Seto, C. *Science* **1991**, *254*, 1312.
(6) Minato, K, I.; Ohkawa, K.; Yamamoto, H. *Macromol. Biosci.* **2006**, *6*, 487.
(7) Sivadasan, K.; Somasundaran, P.; Turro, N, J. *Colloid Polym. Sci.* **1991**, *269*, 131.
(8) Simon, S.; Dugast, J. Y.; Le Cerf, D.; Picton, L.; Muller, G. *Polymer* **2003**, *44*, 7917.
(9) MacKnight, W. J.; Ponomarenko, E. A.; Tirrell, D. A. *Acc. Chem. Res.* **1998**, *31*, 781.
(10) Tazuke, S.; Matsuyama, Y. *Macromolecules* **1975**, *8*, 280.
(11) Kojima, T. *J. Polym. Sci.: Polym. Phys. Ed.* **1980**, *18*, 1685.
(12) Huang, H. Y.; Yun, H.; Lin, H. S.; Kwei, T. K.; Okamoto, Y. *Macromolecules* **1999**, *32*, 8089.
(13) Shogbon, C, B.; Brousseau, J. L.; Zhang, H.; Benicewicz, B. C.; Akpalu, Y. *Macromolecules* **2006**, *39*, 9409.
(14) Musto, P.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1991**, *24*, 4762.
(15) Deimede, V.; Voyiatzis, G. A.; Kallitsis, J. K.; Qingfeng, L.; Bjerrum, N. J. *Macromolecules* **2000**, *33*, 7609.
(16) Choe, E. W.; Choe, D. D. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: New York, 1996.
(17) Savinell, R.; Yeager, E.; Tryk, D.; Landau, U.; Wainright, J.; Weng, D.; Lux, K.; Litt, M.; Rogers, C. *J. Electrochem. Soc.* **1994**, *141*, L46.
(18) Samms, S. R.; Savinell, R. F. *J. Electrochem. Soc.* **1996**, *143*, 1225.
(19) Weng, D.; Wainright, J. S.; Landau, U.; Savinell, R. F. *J. Electrochem. Soc.* **1996**, *143*, 1260.
(20) Mecerreyes, D.; Grande, H.; Miguel, O.; Ochoteco, E.; Marcilla, R.; Cantero, I. *Chem. Mater.* **2004**, *16*, 604.
(21) Xiao, L.; Zhang, H.; Jana, T.; Scanlon, E.; Chen, R.; Choe, E.-W.; Ramanathan, L. S.; Yu, S.; Benicewicz, B. C. *Fuel Cells* **2005**, *5*, 287.
(22) Xiao, L.; Zhang, H.; Scanlon, E.; Ramanathan, L. S.; Choe, E.-W.; Rogers, D.; Apple, T.; Benicewicz, B. C. *Chem. Mater.* **2005**, *17*, 5328.
(23) Sannigrahi, A.; Arunbabu, D.; Jana, T. *Macromol. Rapid Commun.* **2006**, *27*, 1962.
(24) Aspler, J. S.; Guillet, J. E. *Macromolecules* **1979**, *12*, 1082.
(25) Gupta, M. C.; Gupta, A.; Horwitz, J.; Kliger, D. *Macromolecules* **1982**, *15*, 1372.
(26) Gatica, N.; Marcelo, G.; Mendicuti, F. *Polymer* **2006**, *47*, 7397.
(27) Cuniberti, C.; Perico, A.; *Eur. Polym. J.* **1980**, *16*, 887.
(28) Fox, R. B.; Price, T. R.; Cozzens, R. F.; Mcdonald, J. R. *J. Chem. Phys.* **1972**, *57*, 534.
(29) Ravindranath, R.; Vijilaa, C.; Ajikumar, P. K.; Hussain, F. S. J.; Ng, K. L.; Wang, H.; Jin, C. S.; Knoll, W.; Valiyaveettil, S. *J. Phys. Chem. B* **2006**, *110*, 25958.
(30) Fujimura, T.; Tsuchiya, M.; Koizumi, T.; Ishimaru, K.; Kojima, T. *J. Appl. Polym. Sci.* **2003**, *89*, 1412.
(31) Boydston, A. J.; Williams, K. A.; Bielawski, C, W. *J. Am. Chem. Soc.* **2005**, *127*, 12496.
(32) Neuse, E. W. *Adv. Polym. Sci.* **1982**, *47*, 1.
(33) Zimmermann, H.; Joop, N. *Ber. Bunsen-Ges. Phys. Chem.* **1962**, *66*, 342.
(34) Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin/Cummings Pub. Com. Inc.: San Francisco, CA, 1978.
(35) Samanta, A. *J. Phys. Chem. B* **2006**, *110*, 13704.
(36) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; Blackwell Sci. pubs.: Oxford, U.K., 1991.
(37) Liu, G.; Guillet, J. E. *Macromolecules* **1990**, *23*, 4292.
(38) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970.
(39) Hong, P. D.; Chou. C. M.; He, C. H. *Polymer* **2001**, *42*, 6105.
(40) Sun, S. F. *Physical Chemistry of Macromolecules: Basic Principles and Issues*; John Wiley & sons, Inc.: New York, 1994.
(41) Kojima, T. *J. Polym. Sci.: Polym. Phys. Ed.* **1980**, *18*, 1791.
(42) Ryan, M. T.; Helminiak, T. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.*) **1973**, *14*, 1317.
(43) Kojima, T.; Yokota, R.; Kochi, M.; Kambe, H. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1673.

MA070049Q