Role of Solvent Protic Character on the Aggregation Behavior of Polybenzimidazole in Solution

Sandip Ghosh, Arindam Sannigrahi, Sudhangshu Maity, and Tushar Jana*

School of Chemistry, University of Hyderabad, Hyderabad, India

Received: November 13, 2009; Revised Manuscript Received: January 27, 2010

The aggregation behavior of poly(4,4′-diphenylether-5,5′-bibenzimidazole) (OPBI) in polar aprotic (dimethyl acetamide, DMAc) and protic (formic acid, FA) solvents is studied as a function of the polymer concentration and solution temperature. The effects of solvent protic character on the aggregation behavior of OPBI are elucidated. The photophysical studies suggest that the OPBI chains form aggregated structures in both DMAc and FA solutions when the OPBI concentration is increased. The dependences of the emission spectra on the polymer concentrations in two solvents are not similar in nature, indicating that in both of the solvents the aggregations are intermolecular processes, though their mechanisms are different owing to the polyelectrolytic nature of OPBI in FA medium. The triexponential decay profiles obtained from the time-resolved fluorescence study for the concentrated solutions (both in DMAc and FA) display a negative fractional coefficient and longer excited state lifetime, providing support for the aggregations at higher concentration. The temperature dependence emission spectra suggest that the aggregations in both of the solvents destabilize with increasing temperature. The higher activation energy of aggregation (E_A) in DMAc (5.62 KJ/mol) compared with that in FA (3.07 kJ/mol) reveals that the aggregation formation pathways are different in two solvents and stronger aggregates are formed in the former solvent. The dilute solution viscometry (DSV) studies demonstrate that the OPBI chains adapt a bigger extended conformation in FA compared with DMAc owing to the stronger intramolecular chain repulsion in FA arising due to the polyelectrolyte nature of OPBI in this solvent. A conformation transition of OPBI chains from compact collapsed to extended conformer is observed in DMAc solvent with increasing concentration, whereas any such transition is absent in FA medium. Transmission electron microscope (TEM) images and circular dichroism (CD) spectra are also in agreement with the presence of a conformational transition in DMAc and the absence of it in FA. The temperature dependent DSV studies further support the disruption of aggregated structure with increasing temperature in both of the solvents. DSV studies exhibit that the deaggregation is driven by a conformation transition (extended to compact collapsed) in DMAc, whereas in FA the disruption happens without conformational transition.

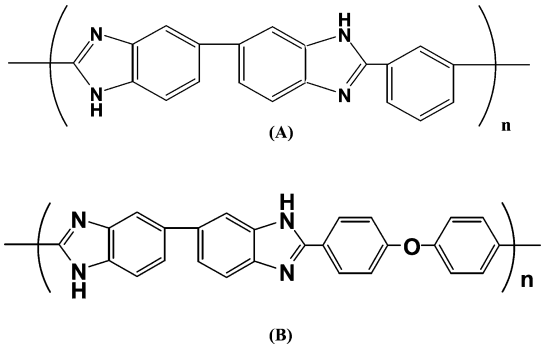
Introduction

Molecular aggregation of polymers and biopolymers in solution represents an important phenomenon in material science and molecular biology. These macromolecules have capabilities to form self-organized structures by interacting with each other in solution and solid state. The self-organization of the macromolecules is predominantly driven by inter- and intramolecular interactions such as hydrogen bonding, electrostatic, van der Waals, and hydrophobic interactions.[1−3] All of these driving forces for the self-organization processes are noncovalent type interactions, and hence, these processes become reversible in nature with concentration, temperature, etc.[4] The molecular aggregated structures of macromolecules created from the self-organization process display very fascinating molecular properties, and these properties can be altered as per the desire by tuning the nature and extent of the self-organization process. Self-organizing systems are widely represented in nature, such as double-helical structures of nucleic acids and bilayers of lipids within the cell membranes.[5−7] There are plenty of investigations reported in the literature on the molecular aggregation of the synthetic polymers.[5,6,8−11] However, most of these reports were focused on vinyl polymers, polypeptides, and other simple structure polymers.[5,6,8−11] MacKnight et al. have demonstrated and studied extensively the polymer chain conformation, conformational transition due to self-organization in the case of polyelectrolyte−surfactant complexes in the solution.[12] The aggregation of synthetic polymers in solutions, polyelectrolyte/surfactant complexes were also studied extensively by Guenet and co-workers.[13] A very limited number of efforts have been attempted in recent years to study the aggregation behavior of the polymers in solution with highly complex molecular structure.[14−17] Very recently, we have carried out a systematic study on the aggregation behavior of meta structured polybenzimidazole (meta-PBI) (Scheme 1A) in polar aprotic solvent, dimethyl acetamide (DMAc).[14] Our group has demonstrated that the polybenzimidazole (*m*-PBI) chains undergo a coil- to rodlike conformational transition in solution with increasing concentration due to the molecular aggregation driven by the self-organization process. The degree of molecular aggregation is strongly dependent upon the molecular orientations of the polymer chains as well as the nature of the solvent.[18,19] Very few attempts have been made in the literature to study the effect of solvents on the aggregation behavior of the macromolecules, and those are mostly with vinyl polymers such as polyvinyl alcohol, etc.[18] However, per our knowledge, there have been no attempts in the literature to date for heterocyclic polymers,

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

10.1021/jp910808u
Published on Web 02/11/2010

SCHEME 1: (A) Poly(2,2′-(*m*-phenylene)-5,5′-bibenzimidazole) (*m*-PBI) and (B) Poly(4,4′-diphenylether-5,5′-bibenzimidazole) (OPBI)



such as polybenzimidazole. Hence, it becomes absolutely necessary to study the effects of solvents on the aggregation behavior of the polybenzimidazole.

Polybenzimidazole (*m*-PBI, Scheme 1A), known as Celazole, is an aromatic heterocyclic polymer which is resistant to strong acids, bases, a variety of chemicals, and high temperatures. Due to these unique properties, PBI is being used in numerous areas, especially in high temperature applications, reverse osmosis membranes, fire-resistant materials, ultrafilters, and other types of separatory media.[20] PBI possesses both proton donor (—NH—) and acceptor (—N═) hydrogen bonding sites which favor the formation of the miscible blends[21−23] with a variety of polymers and also exhibit specific interaction with both protic and aprotic polar solvents.[16,24,25] Phosphoric acid (PA) doped PBI membrane is a promising candidate to prepare cheap and high performance polymer electrolyte membrane materials for polymer electrolyte membrane fuel cells (PEMFCs).[26−29] Several methods have been developed for the fabrication of PA doped PBI membranes.[25,27−31] The superiorities of the membranes obtained from many of these methods relied on the interactions of PBI chains with the solvent molecules in which the PBI molecules are dissolved.[25,31] Earlier, we had demonstrated that PBI chains form aggregated structure in the DMAc solution with increasing concentrations and we have observed a conformational transition during the aggregation process.[14] This above study helped us to design and develop the thermoreversible gel of PBI in PA from where we could fabricate PBI membrane with very high PA loading.[25] Our goal of this Article is to study the aggregation behavior of poly(4,4′-diphenylether-5,5′-bibenzimidazole) (OPBI) (Scheme 1B) in polar protic formic acid (FA) and polar aprotic *N*,*N*-dimethyl acetamide (DMAc) solvents. For the current study, we have chosen OPBI (Scheme 1B) instead of *m*-PBI (Scheme 1A) due to the flexible nature of the OPBI arising for the ether linkage in the OPBI polymer backbone.[32,33] OPBI has very good solubility in both polar protic and aprotic solvents such as FA, DMAc, etc. In this Article, we wish to study the effect of solvents on the OPBI aggregation behavior and also want to explore the possible outcome due to the flexible nature of OPBI on the aggregation. This study may give us a clue to prepare a superior quality of OPBI membrane in protic solvent.

Photophysical studies of polymers have been utilized as a potential approach for the exploration of inter- and intramolecular interactions and molecular motions of the polymer chains and their aggregations.[9,11,16,17,19,34−41] These photophysical studies showed that most of the vinylic polymers bearing aromatic side groups such as styrene, vinylnaphthalene, vinylanthracene, *N*-vinylcarbazole, vinylpyrene, and their copolymers form inter- and intramolecular excimers and exciplexes.[38−42] These excimers and exciplexes were used as a degree of molecular interactions. Huang et al. reported that polyquinolines form excimers in acidic solution, resulting in concentration quenching, and showed that excimer formation is forbidden by intermolecular repulsion between the polymer chains.[17] Recently, it has been reported that side chain urethane methacrylate polymer having pendent pyrene units on each side chain form intramolecular excimers in dilute THF solution and form stable intermolecular aggregated structures at higher concentration.[11] Earlier, molecular aggregation of OPBI in DMAc solution due to the overlapping of polymer chains was studied by Kojima et al.[16] However, Kojima could not predict aggregation in FA medium. Hence, there is a lack of enough thorough investigation in the literature on the aggregation behavior of OPBI in different solvents. This detailed study perhaps can guide us about the chain conformation and the nature of OPBI aggregation in various solvents. Therefore, the current study becomes absolutely necessary for the future development of PBI chemistry.

In this Article, we have studied the intra- and intermolecular interactions of dilute OPBI in DMAc and FA solutions by using steady-state and time-resolved fluorescence spectroscopy, viscosity at different temperatures. Also, transmission electron microscopy (TEM) and circular dichroism spectroscopy are employed to understand the morphological and conformational changes of the OPBI chains in solutions.

Experimental Section

Materials. 3,3′,4,4′-tetraaminobiphenyl (TAB, polymer grade), 4,4′-oxybis(benzoic acid) (OBA), and polyphosphoric acid (PPA, 115%) were purchased from Sigma-Aldrich. Dimethyl acetamide (DMAc) and formic acid (99%) were purchased from Qualigens and SRL India, respectively. All chemicals were used as received.

OPBI Synthesis. The synthesis of OPBI was carried out as per our method reported previously.[33] Briefly, equal moles of TAB and OBA were taken into a three-neck round-bottom flask along with polyphosphoric acid (PPA). The reaction mixture was stirred by using a mechanical overhead stirrer, and a slow stream of purged nitrogen gas was maintained throughout the reaction. The polymerization was carried out at 190−220 °C for approximately 26 h. The OPBI polymer was isolated, neutralized with sodium bicarbonate, washed thoroughly with water, and finally dried in a vacuum oven for 48 h at 100 °C. The dried polymer was characterized by measuring the viscosity in concentrated sulfuric acid (98%) by using a Cannon Ubbelohde capillary dilution viscometer (model F725). The synthesized OPBI has an inherent viscosity (IV) value of 2.29 dL/g at 30 °C. The concentration of the polymer solution for the viscosity measurement was 0.2 g/dL. The intrinsic viscosity ([η]) of the synthesized OPBI was obtained by using the Kuwahra[43] single point method with the help of the following equation

$$[\eta] = \frac{\eta_{sp} + 31n\eta_{rel}}{4C} \quad (1)$$

where η_{sp} and η_{rel} are the specific and relative viscosity of the polymer solution, respectively, and C is the concentration of polymer in g/dL. The calculated intrinsic viscosity for the synthesized OPBI sample using eq 1 was 2.50 dL/g at 30 °C. The viscosity average molecular weight ($\overline{M}_v$) was obtained by using the Mark−Houwnik equation, $[\eta] = K\overline{M}_v^a$, where K =

5.2×10^{-5} dL/g and $a = 0.92$ for H_2SO_4 (98%) solvent at 27 °C.[44] The ($\overline{M_v}$) obtained for the OPBI using the above constants is 21 091.

Dilute Solution Viscometry (DSV). A Cannon Ubbelohde capillary dilution viscometer (model F725) was used to measure the viscosity of OPBI solutions in DMAc and FA. The measurement was carried out at various temperatures (303−343 K) by immersing the viscometer into a temperature controlled water bath. Stock solutions of OPBI were prepared in DMAc and FA. These stock solutions were filtered through the 0.25 μm PTFE filter membrane to remove any microgels or large contaminants. Final solutions were made by the appropriate dilution of the stock solutions with filtered solvent. Flow time readings were recorded at least three times until the difference between two readings was found to be within 0.5 s. The Huggins equation (2) was utilized to analyze the viscosity data.

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

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_H is the Huggins constant. In the case of FA solution, η_{red} increases with decreasing solution concentration, indicating that the OPBI behaves as a polyelectrolyte in FA solvent.[45] Therefore, the Huggins equation could not be applied to obtain k_H and $[\eta]$. We have utilized the isoionic dilution method to obtain $[\eta]$ and k_H for OPBI in FA.[46] We have used LiBr as a salt for the isoionic dilution method.

Spectroscopy. Electronic absorption spectra were recorded on a UV−visible spectrophotometer (model, Cary-100Bio; make, VARIAN). Steady-state fluorescence emission spectra were recorded on a Jobin Yvon Horiba spectrofluorimeter (model Fluoromax-4). A Peltier temperature controller (model LFI-3751) was used for temperature dependent study. Time-resolved fluorescence measurements were carried out using a time-correlated single-photon counting (TCSPC) spectrophotometer (IBH Nano LED). A diode laser ($\lambda_{exc} = 374$ nm) was used as the excitation source, and the instrument response time was 75 ps (fwhm). The emission was detected at a 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. The circular dichroism (CD) spectra of polymer solutions were recorded on a spectropolarimeter (Jasco-810) at 30 °C using a 2 mm quartz cuvette.

Microscopy. A transmission electron microscope (TEM, FEI Tecnai Model No. 2083) operating at 120 kV was used to study the morphological features of the OPBI samples prepared from the various solution concentrations in both DMAc and FA solvents. The TEM samples were prepared by dropping the appropriate concentrated solutions in a carbon coated copper (200 mesh) grid and then scanned for imaging in TEM.

Results and Discussion

Absorption Spectroscopy. The absorption spectra of OPBI (Scheme 1B) solutions in two different solvents, namely, dimethyl acetamide (DMAc, polar aprotic solvent) and formic acid (FA, polar protic solvent), are studied. OPBI solutions of two different concentrations (0.2 g/dL or 5×10^{-3} M and 2×10^{-3} g/dL or 5×10^{-5} M) in both of the solvents are prepared, and their absorption spectra are presented in Figure 1. The OPBI concentrations in molar concentration units are calculated by considering one repeat unit molecular weight as 1 mol of OPBI. In both of the solvent systems, the absorption bands (λ_{max}) of the OPBI dilute solutions owing to the $\Pi \rightarrow \Pi^*$ transitions of the imidazole moiety are observed at 345 nm. Therefore, it is noted that the λ_{max} value for the $\Pi \rightarrow \Pi^*$ transition does not differ for the two solvents used in this study. This observation is in agreement with the previous reports.[47,48] However, the longer wavelength absorption band (low energy band) due to the $n \rightarrow \Pi^*$ transition of the imidazole ring depends on the solvents (Figure 1). In the case of DMAc solution (0.2 g/dL), the $n \rightarrow \Pi^*$ transition is observed at 440 nm, whereas the same transition band appears as dual bands at 424 and 482 nm in the case of FA solution (0.2 g/dL). The reason for this solvent dependence is because of the fact that the FA is a protic solvent which consumes the nonbonding electron available in the nitrogen atoms of the imidazole rings present in the OPBI polymer backbone and yielding an imidazolium cationic species. Hence, in FA medium, the nature of the $n \rightarrow \Pi^*$ transition is significantly different from the DMAc medium. It must be noted that all of the OPBI spectra presented in Figure 1 exhibit a very long tail toward the higher wavelength which becomes more prominent as the concentration of the solution increases. This observation implies the possibility of aggregation of the OPBI polymer chains.[14] A careful comparison between the DMAc and FA spectra for the higher concentration (0.2 g/dL) OPBI solutions shows significant differences between the two spectra in the higher wavelength region, suggesting that the nature of the OPBI polymer chain aggregation in the two solvents is not of similar type. This is quite logical considering the fact that the protic solvent FA produces polyelectrolyte species in the solution[16,25] whereas DMAc does not. A more detailed discussion will follow in a later section in this Article.

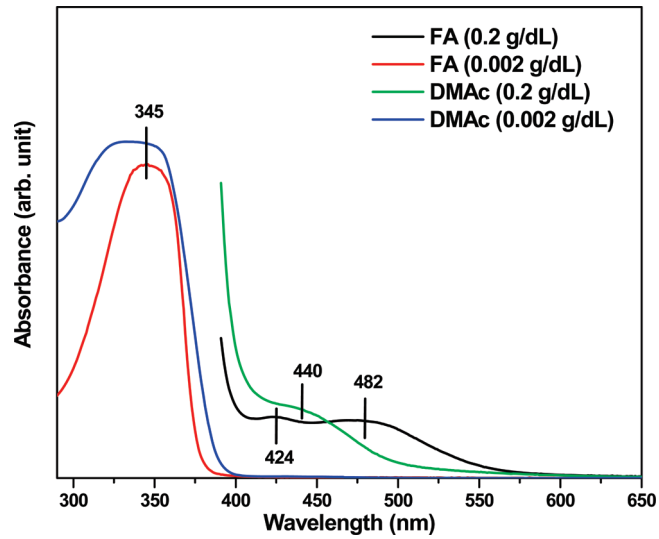


Figure 1. Absorption spectra of OPBI solutions in formic acid (FA) and dimethyl acetamide (DMAc). The concentrations of the solutions are shown in the figure. The spectra are recorded using a cuvette with 1 cm path length.

Steady-State Fluorescence Spectroscopy. Studies of molecular aggregation of polybenzimidazole (*m*-PBI, Scheme 1A) in solution using fluorescence spectroscopy have been reported in the literature, and the emission bands (398 and 410 nm) are assigned to the 0−0 and 0−1 transitions from the excited ^1L_b state of the benzimidazole rings present in the *m*-PBI chain.[16,49]

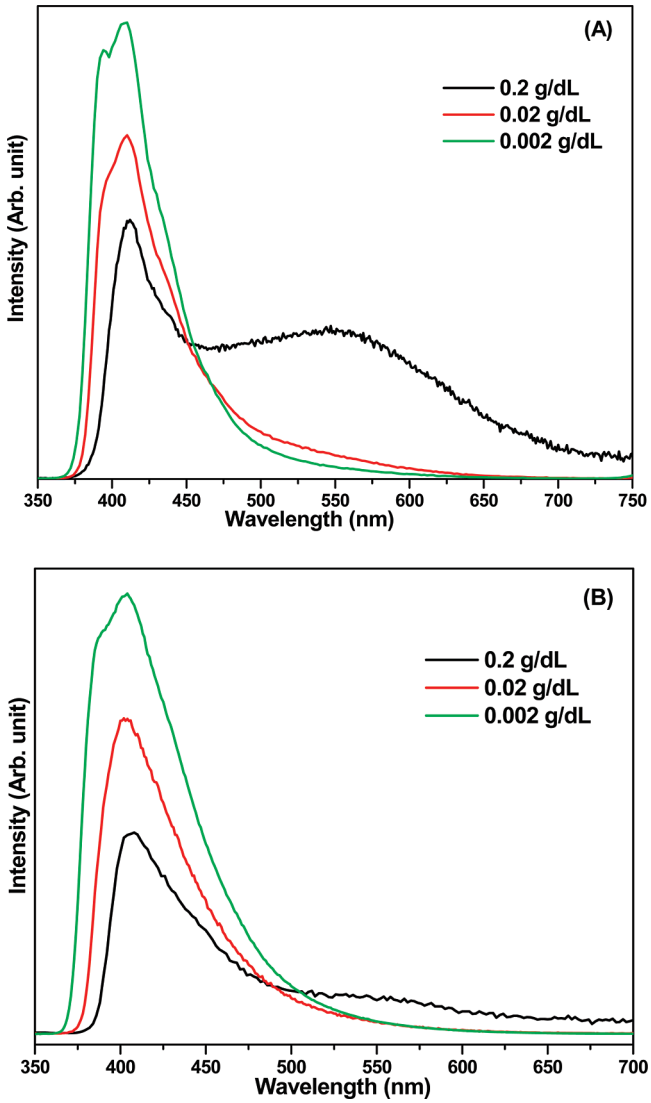


Figure 2. Steady-state fluorescence emission spectra of OPBI in (A) DMAc and (B) FA solution at their indicated concentrations. The excitation wavelength (λ_{exc}) for all of these emission spectra is 340 nm.

Figure 2 represents the emission spectra of OPBI solutions in DMAc and FA at various concentrations. The spectral nature, shapes, and their concentration dependence are consistent with the previous reports on *m*-PBI.[14,16,33] The presence of concentration quenching of OPBI, i.e., the decrease of emission intensity with increasing OPBI solution concentration, is observed in both of the solvents (Figure 2), suggesting the formation of aggregated structures of the OPBI chains in both of the solvents at higher concentrations. Very recently, we observed a similar kind of spectral feature for *m*-PBI in DMAc solution and confirmed conformational transition (compact coil to extended helical rodlike) of the *m*-PBI chains due to the molecular aggregation of the polymer chains with increasing concentration in solution.[14] Earlier, Kojima[16] showed that the critical quenching volume for OPBI chains in DMAc is greater compared to the OPBI chains in FA and suggested very negligible or almost zero aggregation in the FA medium. However, our observation is not in agreement with the Kojima report and we have observed aggregations of OPBI chains both in DMAc and in FA mediums. We believe the nature of the aggregation processes in two different solvents is not similar and hence a thorough comparison of the aggregation behaviors in the two solvents is

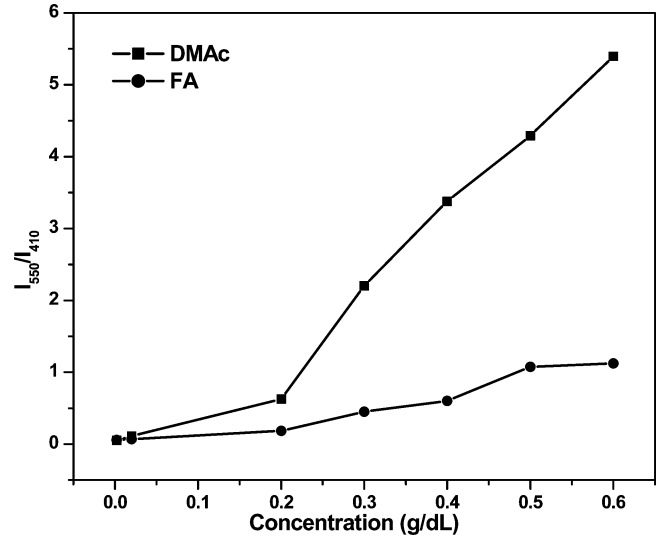


Figure 3. Dependence of longer wavelength (550 nm) to lower wavelength (410 nm) intensity ratio (I_{550}/I_{410}) on the concentration of OPBI in DMAc and FA solutions.

absolutely necessary. A broad emission peak at longer wavelength (~550 nm) appears with increasing concentration of the OPBI solution in both of the solvent systems, as observed in Figure 2A and B. In our previous studies on the aggregation behavior of *m*-PBI solution in DMAc, we have assigned this longer wavelength peak (~550 nm) to the intermolecular aggregation/excimer formation at higher concentration. It must be noted from Figure 2 that the increase of the longer wavelength (~550 nm) peak intensity with increasing solution concentration is very much prominent for the DMAc solution compared to the FA solution. Figure 3 represents a plot of the intensity ratio (I_{550}/I_{410}) between the longer wavelength (550 nm) and lower wavelength (410 nm) emission bands against the solution concentration. A linear increase of the intensity ratio (I_{550}/I_{410}) with the concentration of the solution is observed in the case of the DMAc solution, whereas a negligible concentration dependence is obtained for the FA solution. The observation for the DMAc solution is in agreement with our previous results, hence indicating the presence of intermolecular aggregation of OPBI chains in DMAc solution at higher concentration. On the other hand, the Figure 3 result for OPBI in FA solution brings two obvious conclusions: either the aggregation of OPBI chains in FA is not intermolecular or OPBI chains do not form any aggregated structure in the FA solution. Incidentally, the later conclusion was also drawn by Kojima previously.[16] At this point, it becomes necessary to validate the later conclusion. If the later conclusion drawn by Kojima is found to be wrong, then efforts should be made to understand the nature of aggregation of OPBI chains in the FA solution, which has to be remarkably different from the aggregation of OPBI chains in the DMAc solution.

Long tails in the absorption spectra in both of the solvent systems (Figure 1) are attributed to the presence of aggregated species in the ground state that are energetically different. Also, significant differences are seen in the nature of the long absorption tails between the solvent systems, indicating the presence of different kinds of aggregated species in two different solvents. Each of these aggregated species is characterized by its own absorption and emission maxima. Hence, when the excitation wavelength (λ_{exc}) is shifted, a different species is excited and an emission characteristic of that species is obtained. Therefore, if the fluorescence emission (λ_{em}) of OPBI solution in any particular solvent depends upon the excitation wavelength

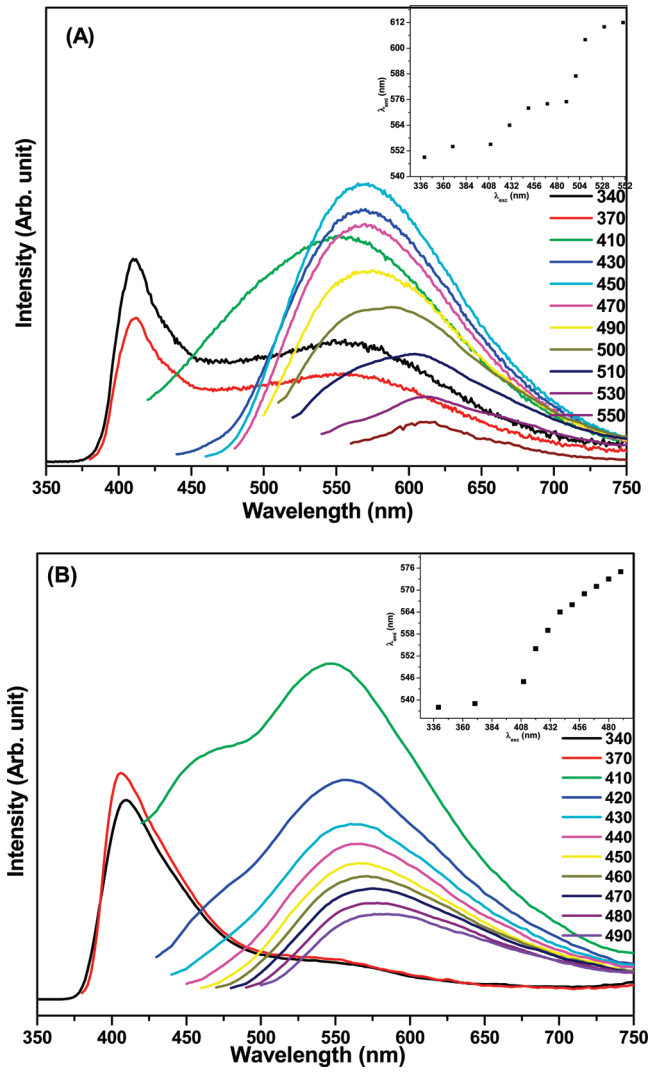


Figure 4. Dependence of steady-state fluorescence emission spectra on the excitation wavelength (indicated in the figure) for OPBI in (A) DMAc and (B) FA solution (the concentrations of both of the solutions is 0.2 g/dL). Inset: plot of λ_{em} against λ_{exc}.

(λ_{exc}), then it can be concluded that the OPBI chains are forming an aggregated structure in that solvent. On the basis of this argument, we have studied the dependence of fluorescence emission on excitation wavelength for OPBI in both DMAc and FA solutions and the results are presented in Figure 4. The emission maxima gradually shift toward longer wavelength with the change in the excitation wavelength. The dependence of λ_{em} on λ_{exc} is presented in the insets of Figure 4. λ_{em} is highly dependent on λ_{exc} in the case of both solvent systems, as observed in Figure 4 (insets). These results clearly show that the OPBI aggregation is taking place in both of the solvents at higher concentration. Therefore, the presence of OPBI aggregation in both of the solvents is confirmed. Hence, the conclusion, "OPBI chains do not form any aggregated structure in FA solution", obtained from Figure 3 and also suggested by Kojima[16] is not correct. Indeed, OPBI chains form aggregated structure in FA solution. However, the Figure 3 results clearly suggest that aggregation of OPBI in FA is not intermolecular in nature, since I_{550}/I_{410} is almost independent of the solution concentration. On the other hand, intermolecular aggregation is observed in the case of DMAc solution which is in agreement with our previous observation.[14] Also, it is worthwhile to note that the extent and nature of λ_{em} dependence on λ_{exc} is not similar for the two solvents (insets of Figure 4). These observations attribute that the nature of the aggregation process is not similar in both of the solvent systems. Now the following question arises: if the OPBI aggregation in FA solvent is not intermolecular in nature (as evident from Figure 3), then how do the OPBI chains form aggregated structure with increasing concentration in the FA solution? The immediate answer to this question would be "the aggregation is intramolecular". However, intramolecular aggregation is not possible in this case, since the different parts of OPBI chains repel each other due to the polyelectrolyte nature of the chain in FA.[50] Also, it must be noted that the changes in the photophysical features of the OPBI in FA solutions are observed only when the concentrations of the solutions are gradually increased. Hence, the aggregation of the OPBI in FA indeed is an intermolecular process, although it does not show the concentration dependence in Figure 3. The reason behind the concentration independency in Figure 3 may be explained by considering the polyelectrolyte nature of OPBI in FA. The OPBI chains repel each other for the polyelectrolyte nature, and simultaneously, the chains try to overlap each other due to the intermolecular attraction arising from the hydrogen bonding of OPBI chains with the FA solvent molecules.[25] Hence, the system compromises itself to a balanced situation and as a result of this we do not see the concentration dependency, although the aggregation is intermolecular. In a later section of this Article, we have made efforts to proof the intermolecular aggregation of OPBI in FA using viscometric results.

Time-Resolved Fluorescence Spectroscopy. We have carried out time-resolved fluorescence lifetime measurements of OPBI in DMAc and FA solutions at dilute (0.002 g/dL) and high (0.2 g/dL) concentrations. The decay profiles of all OPBI solutions are recorded by exciting the samples at 374 nm and monitoring the fluorescence at 417 nm. The decay profiles of OPBI in DMAc and FA solutions are presented in Figure 5A,B and Figure 5C,D, respectively. The decay and best fit parameters for all of the samples are presented in Table 1. The data recorded and shown in Figure 5 for all of the samples are fit quite well, as is evident from the quality of fitting parameter (χ^2) presented in Table 1. All of the decay profiles for OPBI solutions exhibit a triexponential decay function, as is evident from Table 1. A triexponential decay behavior for *m*-PBI solution in DMAc has been reported by us recently. A negative fractional contribution (α_1) is obtained from the concentrated solutions in both of the solvent systems (Table 1), which is attributed to the fact that the decay behavior for the concentrated solutions is different from that of the dilute solution.[51] Figure 5 clearly shows that the nature of the decay profiles for the concentrated solutions is quite different from that of the corresponding dilute solutions. The measured excited state lifetime for the concentrated solutions in both of the solvents are longer than the dilute solutions (Table 1). Previously, we observed a longer excited state lifetime, negative pre-exponential factor (fractional contribution), and growth in decay profile in the case of concentrated *m*-PBI solution in DMAc where the *m*-PBI chains are aggregated.[14] Therefore, based on previous observation and the results obtained (Figure 5 and Table 1) from the time-resolved fluorescence lifetime measurement of OPBI in DMAc and FA solutions at dilute (0.002 g/dL) and high (0.2 g/dL) concentrations, we can conclude that OPBI chains aggregate at higher concentration in both DMAc and FA media. The excited state lifetime (τ_{av}) for dilute solution (0.002 g/dL) in both of the solvents are almost the same; however, τ_{av} for concentrated solution (0.2 g/dL) in DMAc (1708 ps) is significantly longer than that for the FA solution (1271 ps) at an identical

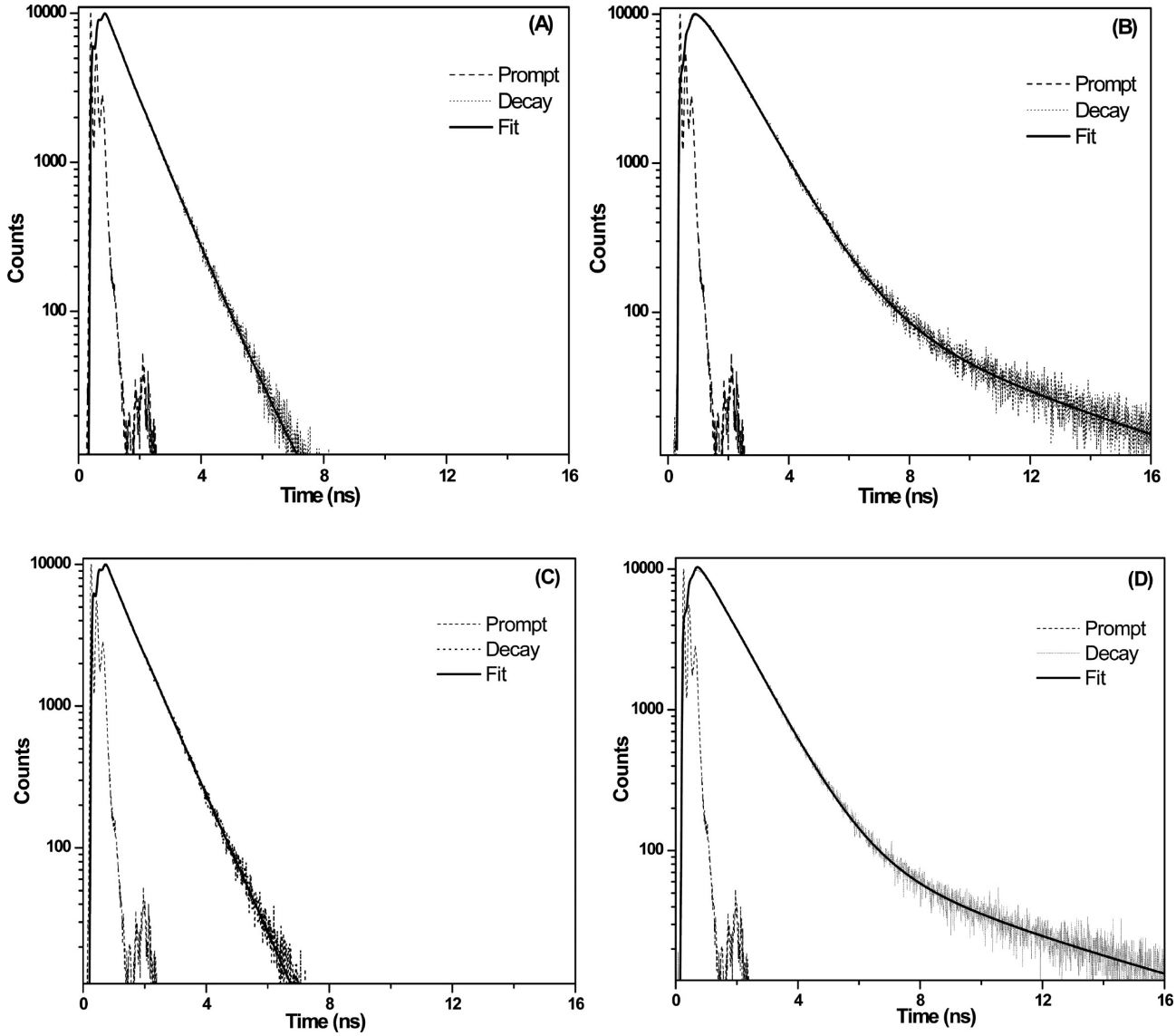


Figure 5. Time-resolved fluorescence decay profiles of OPBI in DMAc and FA solutions: (A) 0.002 g/dL in DMAc; (B) 0.2 g/dL in DMAc; (C) 0.002 g/dL in FA; (D) 0.2 g/dL in FA. $\lambda_{exc} = 374$ nm.

TABLE 1: Fluorescence Decay Parameters for OPBI in DMAc and FA Solutions at Different Concentrations[a]

PBI concentration (g/dL)	τ_1 (ps)	α_1	τ_2 (ps)	α_2	τ_3 (ps)	α_3	τ_{avg} (ps)	χ^2
0.002 in DMAc	596	0.277	960	0.37	78	0.352	548	1.153
0.2 in DMAc	448	–0.685	1147	1.665	5321	0.0197	1708	1.338
0.002 in FA	480	0.138	909	0.461	79	0.399	518	1.245
0.2 in FA	513	–0.331	1036	1.317	5589	0.0135	1271	1.721

[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_{avg}), and the quality of fitting (χ^2) for the data in Figure 5 are shown.

concentration (Table 1). This difference in excited state lifetime indicates that the nature of the aggregations in the two solvent systems is not similar.

Temperature Dependent Fluorescence Spectroscopy. In the previous sections, we have demonstrated that the OPBI chains form aggregated structure at higher concentration in both the FA and DMAc media. The nature of the aggregations in these two solvents is different owing to the fact that the OPBI acts as a polyelectrolyte in the acidic medium (FA), whereas it is not a polyelectrolyte in DMAc. Figure 6 compares the steady-state fluorescence emission intensity of OPBI solution (0.2 g/dL) in

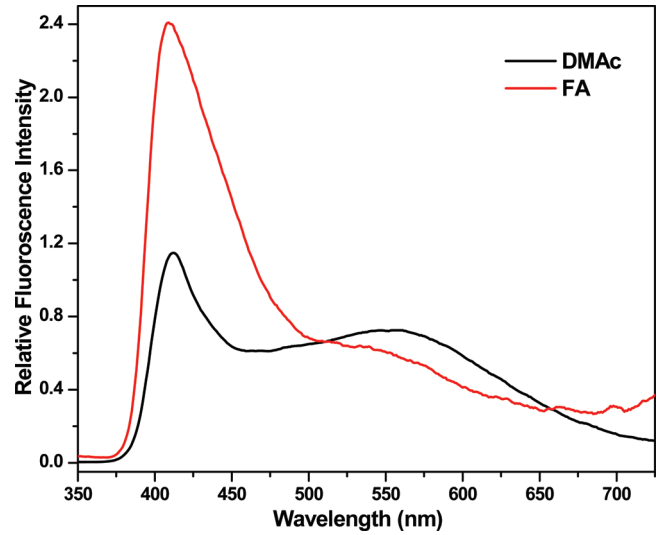


Figure 6. Steady-state fluorescence emission spectra of OPBI solution in FA and DMAc. The concentration of both of the solutions is kept constant at 0.2 g/dL.

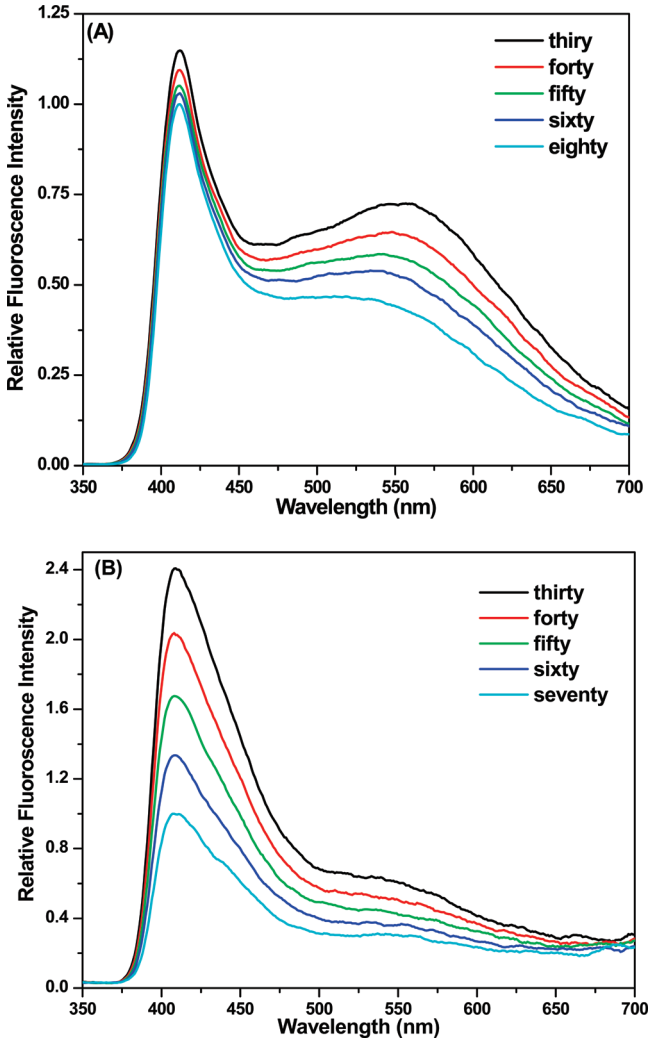


Figure 7. Temperature dependent fluorescence emission spectra of OPBI solution (0.2 g/dL) in (A) DMAc and (B) FA.

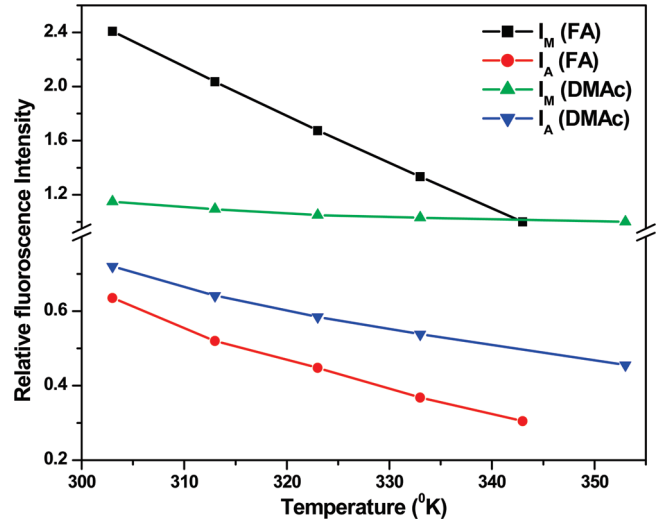


Figure 8. Dependence of monomer (I_M) and aggregate (I_A) intensities of OPBI solution (0.2 g/dL) in FA and DMAc with temperature.

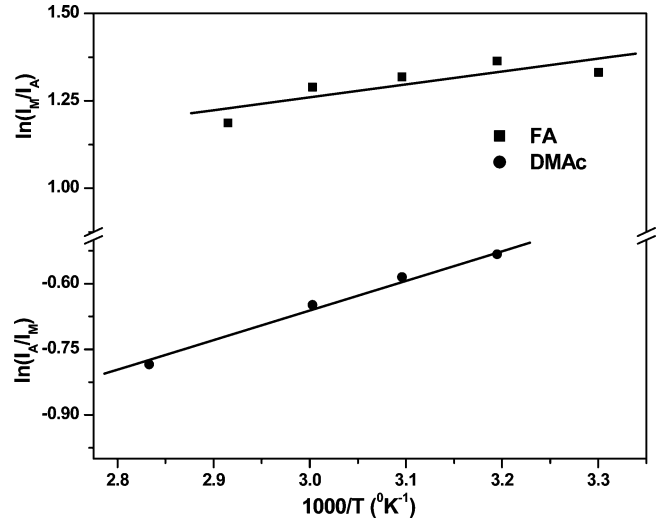


Figure 9. Arrhenius plots for activation energies of the OPBI solutions (0.2 g/dL) in FA and DMAc.

FA and DMAc. At an exactly identical solution concentration (0.2 g/dL), the emission intensity for FA solution is much higher than that of DMAc solution (Figure 6). The larger emission intensity attributes the fact that the access to the chromophoric units (here, the imidazole moiety) is easier in the case of FA compared to the case of DMAc. The OPBI chains in FA medium repel each other and stay apart due to the polyelectrolyte nature, and therefore, the choromophoric imidazole units are more exposed and easily accessible. On the other hand, in the case of DMAc, the OPBI chains are more compact and hence the access to the imidazole units is low compared to the FA, resulting in lower emission intensity than the FA.

We have recorded the temperature dependent fluorescence emission spectra of OPBI solution (0.2 g/dL) in FA and DMAc to study the effect of temperature on the aggregation behavior of the OPBI chains in these two different media. The emission intensity decreases with increasing temperature in both cases (Figure 7). This shows that the OPBI chain aggregation is disrupted with increasing temperature. In the earlier sections, we have said that the broad peak at longer wavelength (~550 nm) is due to the fluorescence of the aggregated species (A) of the OPBI chains and the lower wavelength (~410 nm) is the contribution of the molecular/monomer fluorescence (M). Figure 7 clearly suggests that both intensities I_A (fluorescence intensity of aggregates) and I_M (fluorescence intensity of monomer) for both of the solvents decrease with increasing temperature. It is important to note from Figure 8 that the temperature dependence of I_M for FA is much sharper among all others. A strong solvent proton quenching of the imidazole moiety takes place at higher temperature because of the polyelectrolyte nature of the OPBI in FA, and therefore, I_M sharply decreases with increasing temperature in the case of FA solution, as observed in Figure 8. It is evident from Figures 7 and 8 that the OPBI aggregations in both of the solutions are temperature dependent and hence the aggregation processes must obey the Arrhenius relationship with activation energy (E_A) for the processes. E_A can be obtained from the following equation:

$$\frac{I_M}{I_A} = \text{constant} \times e^{-E_A/RT} \qquad (3)$$

where I_A and I_M are the fluorescence intensities for the aggregates and monomer emission, respectively. Hence, the activation energies for the aggregation processes of OPBI in FA and DMAc solutions can be obtained from the suitable plots (Figure 9) of the fluorescence intensities as a function of temperature.[42,52] The activation energies obtained from the Arrhenius plot (Figure 9) are 3.07 and 5.62 kJ/mol for FA and

DMAc solution, respectively. The smaller activation energy for the FA solution than the DMAc solution suggests that in the former case aggregation is not as strong as it is in the later case. The weaker aggregation in the case of FA than the DMAc is indeed due to the polyelectrolyte nature of the OPBI in this medium which directs the OPBI chains to aggregate in a different manner in FA so that it requires smaller energy. Hence, the nature of the aggregation processes of OPBI in both solvents is not similar.

Viscosity Study. The dilute solution viscosity (DSV) studies have been used in the literature very often to assess the interaction between polymer molecules and solvent in the solution.[9,10,18,53] The DSV measurements of polymer solutions give two well-known important parameters: the Huggins constant (k_H) and the intrinsic viscosity ([η]). The values of these two parameters are frequently used to determine the degree of polymer−solvent interactions and the polymer chain conformation in the solution. The intrinsic viscosities ([η]) obtained from the DSV measurements are often used to predict the polymer chain dimension and therefore can be utilized to study the chain conformation in the solution.[53,54] The hydrodynamic radius (R_h) or radius of gyration (R_g) corresponds to the chain dimension of the polymer in solution. The chain dimension (R_h or R_g) for a fixed molecular weight polymer is directly proportional to [η] as per the relation[55] $[\eta] \approx R_g^2 R_h/M$. Hence, smaller [$\eta$] values suggest compact dimensions, whereas bigger [η] values indicate extended dimensions of polymer in solution. Therefore, the above discussion clearly suggests that the value of [η], obtained from the DSV method, can very well predict the chain conformation of polymer in solution. In short, smaller [η] suggests a collapsed compact conformation, whereas an extended conformation is obtained for larger [η] values.

The [η] values obtained from the DSV measurements at 30 °C for OPBI solutions in DMAc and FA are 3.921 and 7.063 dL/g, respectively. The smaller [η] of OPBI solution in DMAc than FA suggests that the OPBI chains exhibit stronger intermolecular interaction in the latter solvent rather than the former one. Hence, the OPBI chains exist in a more extended form in FA than in DMAc. In other words, the chain dimension of OPBI is bigger in FA solvent than DMAc solvent. Hence, OPBI is more swollen in FA than in DMAc. Our spectroscopic studies described in the previous sections demonstrated that the OPBI chains form aggregated structure with increasing polymer concentration in the solution in both of the solvents; however, the nature of the aggregation could be different. We have observed from the DSV measurements that the [η] value is not altered by the concentration of the OPBI solution in FA; in contrast, it increases significantly from lower concentration to higher concentration regions in DMAc solution. The [η] values of OPBI solution in DMAc at 30 °C for the concentration ranges 0.6−0.075 g/dL (higher) and 0.0375−0.0047 g/dL (lower) are 4.659 and 2.585 dL/g, respectively. This result attributes a conformational transition of OPBI chains from compact collapsed conformer to extended conformer in DMAc solution to increasing solution concentration. In contrast, no such conformational transition of OPBI chains is predicted in FA solution with increasing concentration. At lower concentration in DMAc, due to the strong intramolecular interactions between the OPBI chains, the solvent molecules are not able to penetrate inside the polymer coil for swelling, hence resulting in a compact collapsed conformation. However, with increasing concentration, the intermolecular interactions between the OPBI chains are increased significantly, which allows solvent molecules to diffuse inside the coil and produce an extended structure. A

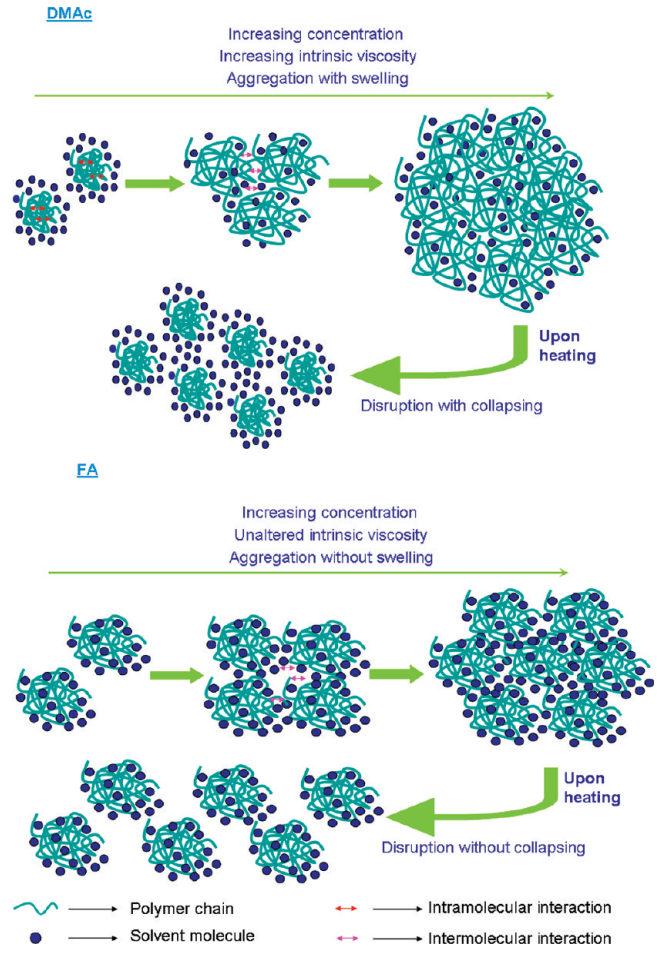


Figure 10. Schematic representation of the aggregation behavior of OPBI in DMAc and FA solvent with increasing concentration. Also, the stability of aggregated structures upon heating is shown.

schematic presentation of this process is depicted in Figure 10. In contrast to the OPBI behavior in DMAc solution, OPBI chains in FA solvent do not show any conformational transition upon aggregation, as depicted in the schematic presentation given in Figure 10. The polyelectrolyte character of the OPBI in FA medium is the driving force for this unaltered conformation. The various parts of the OPBI chains repel each other due to the electrolyte nature which helps the solvent molecule go inside the polymer chain easily and results in an extended conformation even at low concentration. As the concentration increases, interchain repulsion due to polyelectrolytic behavior and interchain attraction owing to the hydrogen bonding attraction between the chains through the solvents molecules[25] oppose each other. Finally, these two opposing forces counter balance each other to get the stabilization and form aggregates without disturbing the chain conformation. Hence, all of the above discussion clearly agrees with our spectroscopic results and proves that the aggregation in both solvents takes place with increasing concentration; however, their mechanisms of formation are different. In the next section, we deal with the morphological features of the OPBI in both of the solvents, arising due to the aggregation process.

Temperature dependent DSV measurements of polymer solution can help us understand the effect of temperature on the polymer chain conformation and the polymer−solvent interaction.[14,56] Recently, we utilized the temperature dependent DSV method to study the stability of the aggregation of *m*-PBI in a polar aprotic solvent such as DMAc.[14] In Figure 11, we

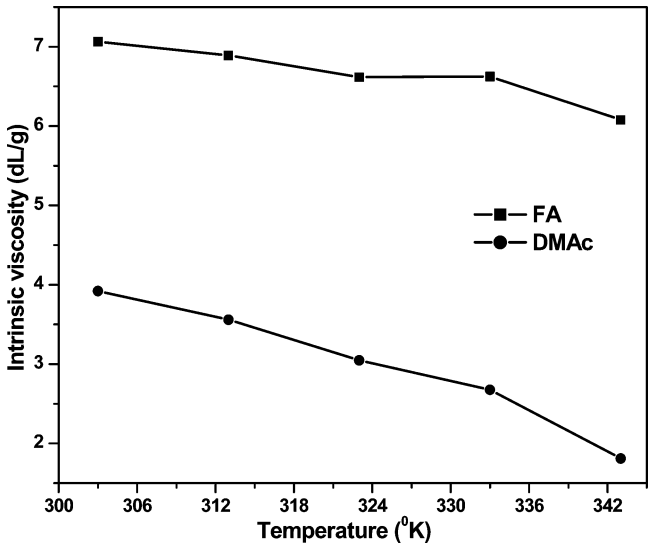


Figure 11. Effect of temperature on the intrinsic viscosity ([η]) of OPBI in FA and DMAc solutions for the concentration region from 0.3 to 0.0375 g/dL.

plotted intrinsic viscosity ([η]) as a function of temperature for OPBI in both solvent systems. The most striking observation in Figure 11 is that [η] does not vary at all with temperature for the FA solvent and, on the other hand, exhibits significant variation with temperature in the case of DMAc medium. Our temperature dependent fluorescence study shows that with increasing temperature aggregation for both cases breaks down. Hence, these results (Figure 11) suggest that the disruption of aggregation in the case of FA is not associated with any conformational transition; however, the disruption of aggregation in DMAc solution is associated with conformational transition (Figure 10). The intrinsic viscosity of OPBI in DMAc solution is much smaller than that in FA for the entire temperature range studied here and decreases sharply with increasing temperature only in the case of DMAc solution (Figure 11). This observation reveals that OPBI chains in FA exhibit a more swollen structure than the DMAc. This result also suggests the presence of a conformational transition in the case of DMAc from extended conformer to compact collapsed structure with increasing temperature, since [η] is temperature dependent, and the absence of any conformational change for FA solution, since [η] is temperature independent in the later case. The schematic diagram presented in Figure 10 describes the aggregation processes, conformational transition, and thermal stability of the aggregates in both solvents. Therefore, all of our above results suggest that the aggregation mechanisms for two different solvents are not similar; in DMAc, the aggregation is driven by conformational transition, whereas, in FA, no transition is observed.

Electron Microscopy. In the above discussions, we have demonstrated that the OPBI chain undergoes a structural conformation transition (compact collapsed to swelled extended) with increasing concentration in DMAc solvent and it exhibits extended dimensions in all of the concentrations in FA solvent, indicating that it does not undergo any conformational transition in this solvent (FA). To strengthen our above observations, we have studied the morphology of the OPBI samples made from dilute (0.002 g/dL) and concentrated (0.2 g/dL) solutions in both DMAc and FA solvents using transmission electron microscopy (TEM). The TEM micrographs of various OPBI samples are presented in Figure 12. The micrograph of the dilute DMAc sample (Figure 12 A) consists of closely packed smaller entities

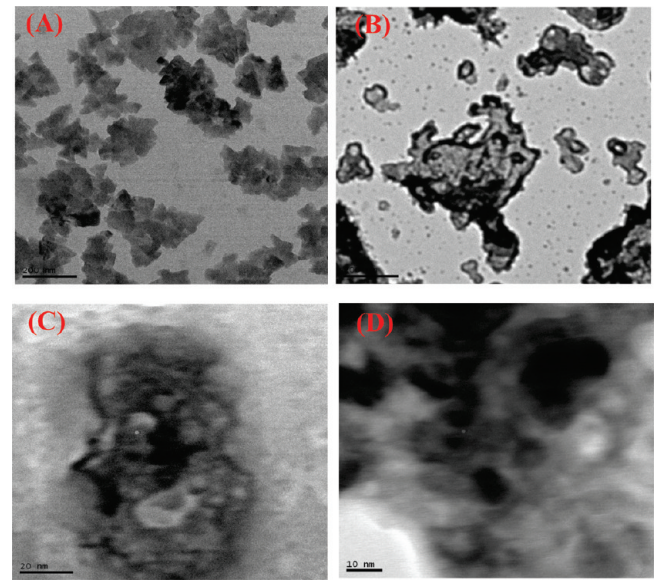


Figure 12. TEM micrographs of OPBI samples made from different concentrations in DMAc and FA: (A) 0.002 g/dL in DMAc; (B) 0.2 g/dL in DMAc; (C) 0.002 g/dL in FA; (D) 0.2 g/dL in FA.

which look like triangles. This is expected, since, at this concentration in DMAc, the OPBI chain exhibits a compact collapsed structure. Figure 12B is the TEM micrograph obtained from the concentrated (0.2 g/dL) OPBI solution in DMAc. The morphological feature of this image is distinctly different from the dilute solution morphology (Figure 12A). This TEM image clearly shows the extended or swelled structures. Hence, our prediction about the conformation transition of OPBI in DMAc solution with increasing concentration is indeed true and has gotten real proof from the TEM study. In contrast to the results obtained for DMAc solutions, the morphological observations are quite different for the samples made from OPBI solution in FA (Figure 12C and D). In these cases, we have obtained the extended structures type morphology in both the case of dilute and concentrated solutions, as observed in the TEM images presented in Figure 12C and D. These TEM results are in agreement with our earlier conclusion that the OPBI does not undergo any conformation structural transition during the aggregation process with increasing solution concentration in FA solvent. Hence, the morphological features of dilute and concentrated solutions in FA are quite similar.

We have also carried out circular dichroism (CD) studies of the OPBI solutions in both solvents to understand and monitor the conformational changes of the OPBI chains. Figure 13 represents the CD spectra of OPBI solutions in FA and DMAc at their indicated concentration. The most important observation that needs to be noted from Figure 13 is that both the dilute and concentrated solutions of OPBI in FA are CD active. However, only the concentrated OPBI solution in DMAc is CD active and dilute solution is inactive. A similar observation for *m*-PBI in DMAc has been observed very recently.[14,24] Thus, the above results clearly are attributed to the fact that OPBI aggregates with increasing concentration both in FA and DMAc but it undergoes a conformational transition in the case of DMAc and not in the case of FA. Hence, we can summarize that the aggregation processes in both solvents do not follow similar mechanisms.

Conclusion

The aggregation behavior of OPBI in polar aprotic solvent such as dimethyl acetamide (DMAc) and polar protic solvent

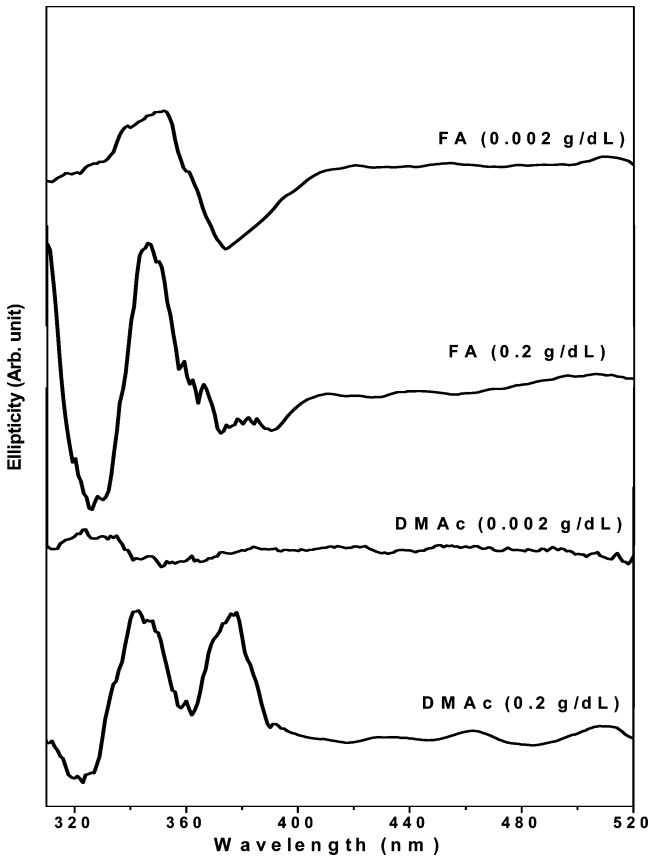


Figure 13. Circular dichroism spectra of OPBI in both DMAc and FA solution at their indicated concentrations.

such as formic acid (FA) is studied by varying the polymer concentration in the solution. The role of solvent protic character on the aggregation behavior of OPBI and the associated conformational transitions are elucidated by employing various methods such as photophysical, dilute solution viscosity (DSV), microscopy, and circular dichroism. Steady-state and time-resolved fluorescence spectroscopy studies demonstrated the formation of an aggregated structure of OPBI chain in both DMAc and FA solvents at higher concentration. The concentration dependent photophysical study proved that the aggregation is an intermolecular process in both solvent systems; however, the mechanisms of aggregate formation in both solvent systems are not similar. It has also been shown that stronger aggregates are formed in DMAc compared to FA solvent, since the activation energy of aggregation (E_A) in DMAc is higher than that in FA. DSV studies revealed that with increasing polymer concentration in solution OPBI chains undergo a conformational transition from a compact collapsed conformer to extended structure in DMAc solvent, whereas no such transition is observed in FA solvent. The presence of strong intramolecular repulsion of OPBI chains in FA due to the polyelectrolyte behavior of OPBI in this solvent is the driving force for the unaltered conformation. TEM images and CD spectra obtained from various polymer concentrations also supported the conformational transition of OPBI in DMAc and the absence of any such transition in FA. The temperature dependent studies (steady-state fluorescence and DSV) proved that the aggregated structure dissociated into nonaggregated species with increasing temperature in both DMAc and FA solvent. Temperature dependent DSV studies confirmed that the disruptions of the aggregates are accompanied by a conformational transition (extended to collapsed) in the case of DMAc, whereas an unaltered conformation is obtained in the case of FA. Therefore, in summary, we can conclude that OPBI chains form aggregated structures in both polar aprotic (DMAc) and polar protic (FA) solvents with increasing polymer concentration in the solutions and these aggregates dissociate at higher temperature in both cases. Most importantly, the nature of the aggregation and its disruptions is driven by different mechanisms due to the protic and aprotic nature of the solvents.

Acknowledgment. We gratefully acknowledge financial support by DST (Grant No. SR/S1/PC-58/2008). We thank Prof. A. Samanta and Mr. D. Khara for helping us with the time-resolved experiments. We sincerely thank Centre for Nanotechnology, University of Hyderabad. for allowing us to use the TEM facility. S.G. thanks CSIR for the senior research fellowship.

References and Notes

(1) Lehn, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89.
(2) Lehn, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.
(3) Ky Hirschberg, J. H. K.; Brunsveld, L.; Ramzi, A.; Vekemans, J. A. J. M.; Sijbesma, R. P.; Meijer, E. W. *Nature* **2000**, *407*, 167.
(4) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Ky Hirschberg, J. H. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601.
(5) Bekturov, E. V.; Bimendina, L. A. *Adv. Polym. Sci.* **1981**, *41*, 99.
(6) Tschuchida, E.; Abe, K. *Adv. Polym. Sci.* **1982**, *45*, 1.
(7) Whitesides, G.; Mathias, J.; Seto, C. *Science* **1991**, *254*, 1312.
(8) Minato, K. I.; Ohkawa, K.; Yamamoto, H. *Macromol. Biosci* **2006**, *6*, 487.
(9) Sivadasan, K.; Somasundaran, P.; Turro, N. J. *Colloid Polym. Sci.* **1991**, *269*, 131.
(10) Simon, S.; Dugast, J. Y.; Le Cerf, D.; Picton, L.; Muller, G. *Polymer* **2003**, *44*, 7917.
(11) Deepak, V. D.; Asha, S. K. *J Phys. Chem. B* **2009**, *113*, 11887.
(12) MacKnight, W. J.; Ponomarenko, E. A.; Tirrell, D. A. *Acc. Chem. Res.* **1998**, *31*, 781.
(13) (a) Reinecke, H.; Fazel, N.; Dosiere, M.; Guenet, J. M. *Macromolecules* **1997**, *30*, 8360. (b) Reinecke, H.; Mijangos, C.; Lòpez, D.; Guenet, J. M. *Macromolecules* **2000**, *33*, 2049. (c) Ray, B.; El Hasri, S.; Guenet, J. M. *Eur. Phys. J. E* **2003**, *11*, 315.
(14) Sannigrahi, A.; Arunbabu, D.; Sankar, R. M.; Jana, T. *Macromolecules* **2007**, *40*, 2844.
(15) Tazuke, S.; Matsuyama, Y. *Macromolecules* **1975**, *8*, 280.
(16) Kojima, T. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1685.
(17) Huang, H. Y.; Yun, H.; Lin, H. S.; Kwei, T. K.; Okamoto, Y. *Macromolecules* **1999**, *32*, 8089.
(18) Hong, P.-D.; Chou, C.-M.; He, C.-H. *Polymer* **2001**, *42*, 6105.
(19) Fakis, M.; Anestopoulos, D.; Giannetas, V.; Persephonis, P. *J. Phys. Chem. B* **2006**, *110*, 24897.
(20) Choe, E. W.; Choe, D. D. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: New York, 1996.
(21) Arunbabu, D.; Sannigrahi, A.; Jana, T. *J. Phys. Chem. B* **2008**, *112*, 5305.
(22) Deimede, V.; Voyiatzis, G. A.; Kallitsis, J. K.; Qingfeng, L.; Bjerrum, N. J. *Macromolecules* **2000**, *33*, 7609.
(23) Musto, P.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1991**, *24*, 4762.
(24) Shogbon, C. B.; Brousseau, J.-L.; Zhang, H.; Benicewicz, B. C.; Akpalu, Y. *Macromolecules* **2006**, *39*, 9409.
(25) Sannigrahi, A.; Arunbabu, D.; Jana, T. *Macromol. Rapid Commun.* **2006**, *27*, 1962.
(26) Hickner, M. A.; Ghassemi, H.; Kim, S. Y.; Einsla, B. R.; McGrath, J. E. *Chem. Rev.* **2004**, *104*, 4587.
(27) 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.
(28) Savinell, R.; Yeager, E.; Tryk, D.; Landau, U.; Wainright, J.; Weng, D.; Lux, K.; Litt, M.; Rogers, C. *J. Electrochem. Soc.* **1994**, *141*, L46.
(29) Samms, S. R.; Wsmus, S.; Savinell, R. F. *J. Electrochem. Soc.* **1996**, *143*, 1225.
(30) Mecerreyes, D.; Grande, H.; Miguel, O.; Ochoteco, E.; Marcilla, R.; Cantero, I. *Chem. Mater.* **2004**, *16*, 604.
(31) Xiao, L.; Zhang, H.; Scanlon, E.; Ramanathan, L. S.; Choe, E. W.; Rogers, D.; Apple, T.; Benicewicz, B. C. *Chem. Mater.* **2005**, *17*, 5328.
(32) Xu, H.; Chen, K.; Guo, X.; Fang, J. *Polymer* **2007**, *48*, 5541.
(33) Sannigrahi, A.; Ghosh, S.; Lalnuntluanga, J.; Jana, T. *J. Appl. Polym. Sci.* **2009**, *111*, 2194.

(34) Marletta, A.; Goncalves, V. C.; Balogh, D. T. *J. Lumin.* **2006**, *116*, 87.

(35) 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.

(36) Traiphol, R.; Charoenthai, N.; Srikhirin, T.; Kerdcharoen, T.; Osotchan, T.; Maturos, T. *Polymer* **2007**, *48*, 813.

(37) Wang, S.; Wu, P.; Han, Z. *Macromolecules* **2003**, *36*, 4567.

(38) Aspler, J. S.; Guillet, J. E. *Macromolecules* **1979**, *12*, 1082.

(39) Gupta, M. C.; Gupta, A.; Horwitz, J.; Kliger, D. *Macromolecules* **1982**, *15*, 1372.

(40) Gatica, N.; Marcelo, G.; Mendicuti, F. *Polymer* **2006**, *47*, 7397.

(41) Cuniberti, C.; Perico, A. *Eur. Polym. J.* **1980**, *16*, 887.

(42) Fox, R. B.; Price, T. R.; Cozzens, R. F.; Mcdonald, J. R. *J. Chem. Phys.* **1972**, *57*, 534.

(43) Kuwahara, N. *J. Polym. Sci.* **1963**, *A1*, 2395.

(44) Yuan, Y.; Johnson, F.; Cabasso, I. *J. Appl. Polym. Sci.* **2009**, *112*, 3436.

(45) Fuoss, R. M. *J. Polym. Sci.* **1948**, *3*, 603.

(46) Nandi, P.; Bhattarai, A.; Das, B. *J. Polym. Sci, Part B: Polym. Phys.* **2007**, *45*, 1765.

(47) Neuse, E. W. *Adv. Polym. Sci.* **1982**, *47*, 1.

(48) Sannigrahi, A.; Arunbabu, D.; Sankar, R. M.; Jana, T. *J. Phys. Chem. B* **2007**, *111*, 12124.

(49) Zimmermann, H.; Joop, N. *Ber. Bunsen-Ges. Phys. Chem.* **1962**, *66*, 342.

(50) The reduced viscosity of the dilute OPBI solution in FA increases sharply and shows a maximum with decreasing concentration, providing support for the polyelectrolytic character of OPBI in FA solvent. The polyelectrolyte behavior of OPBI in FA solution is observed in the entire range of temperature (viz., 30−70 °C) studied here.

(51) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970.

(52) Skilton, P. F.; Ghiggino, K. P. *Polym. Photochem.* **1985**, *5*, 179.

(53) Sun, S. F. *Physical Chemistry of Macromolecules: Basic Principles and Issues*; John Wiley & Sons, Inc.: New York, 1994.

(54) Budhlall, B. M.; Landfester, K.; Sudol, E. D.; Dimonie, V. L.; Klein, A.; El-Aasser, M. S. *Macromolecules* **2003**, *36*, 9477.

(55) Weill, G.; Des Cloiseaux, J. *J. Phys. (Paris)* **1979**, *40*, 99.

(56) Kojima, T.; Yokota, R.; Kochi, M.; Kambe, H. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1673.

JP910808U