Structural Fine-Tuning of (−Donor−*spacer*−acceptor−*spacer*−)$_n$ Type Foldamers. Effect of Spacer Segment Length, Temperature, and Metal-Ion Complexation on the Folding Process

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ABSTRACT: The synthesis of a series of polymers (**PDA—*n*OE**) containing an alternating arrangement of electron rich (donor) and electron deficient (acceptor) aromatic units, which are linked by flexible oligo(oxyethylene) (*n*OE) spacers, is reported. The length of the oligo(oxyethylene) spacer was varied from tetra(oxyethylene) ($n = 4$) to hexa(oxyethylene) ($n = 6$), to examine the relative propensities of these polymers to form folded structures by virtue of intrachain charge-transfer interactions between the adjacent donor and acceptor units. Comparison of the proton NMR and UV−visible spectra of the three different polymers clearly reveals that **PDA—4OE**, which has the shortest tetra(oxyethylene) spacer, exhibits the greatest propensity to fold in the nascent form. A significant upfield shift of the aromatic protons upon lowering of temperature confirmed this greater tendency of the **PDA—4OE** to fold; the spectra of polymers with longer spacers, on the other hand, exhibited a very weak temperature dependence indicating their sluggishness to fold in nascent form. However, in the presence of suitable alkali-metal ions (or a polar solvent), the spectra of the polymers with longer oligo(oxyethylene) spacers also exhibit a much stronger temperature dependence (similar to the **PDA—4OE** case), implying the occurrence of a metal-ion (and solvophobic effect) assisted formation of folded structures. These NMR studies corroborate well with similar variable temperature UV−visible spectral studies, wherein the intensities of the D−A charge-transfer band is monitored as a signature of the folded structure; there were, however, some distinct differences in the nature of the variation in the case of nascent polymer samples that appear to reflect the differences in sensitivities of the two spectral techniques to the folding process. In an effort to better understand the folding process, model compounds of the type donor−*spacer*−acceptor and analogous DAD and ADA were synthesized. Comparison of the spectral changes seen in model compounds, both as a function of temperature and during alkali-metal ion titrations, with those seen in the analogous polymers helped confirm that the folded structures in the polymer clearly must involve intrachain charge-transfer interactions that exceeds simple pairing of adjacent donor and acceptor units; i.e., the acceptors in the folded polymer are sandwiched between donors and vice versa, thereby forming extended stacks.

Introduction

The stupendous growth of supramolecular science into a major discipline that has helped bridge many traditional areas of science, such as chemistry, physics, biology, and material science, stands testimony to the growing importance of weak noncovalent interactions across these various disciplines.[1] Chemistry has been greatly enriched by the recognition that several of these weak interactions can be designed to work cooperatively both to achieve extraordinarily elegant structures as well to perform highly specific functions. While the principles that govern organization of small molecules have been reasonably mastered, designing synthetic polymers that can adopt a specifically targeted secondary structure has been far more difficult.[2] The motivation to generate synthetic polymers with a precisely controlled conformation stems from the desire to emulate the elegance of nature on one hand, while at the same time from the expectation that this will enable one to bridge the gap between the molecular scale and the macroscopic one, in terms of the evolution of structural order.

There has been a great deal of effort during the past decade to understand the essential design elements that would enable secondary structure formation in synthetic macromolecules through intrachain, intersegment interactions. Gellman[3] first used the term "*foldamer*" to describe "any polymer with a strong tendency to adopt a specific compact conformation", which was more recently elaborated upon by Moore and co-workers in a very comprehensive review.[4] During the past decade, several classes of abiotic oligomers that adopt folded conformations in solution have been developed. Examples of such systems are oligocarbamates,[5] oligopyrrolidones,[6] oligoureas,[7] carbohydrate oligomers,[8] oligoanthrilamides,[9] crescent oligoamides,[10] oligo(*m*-phenylene ethynylene)s,[11] pyrimidine−pyridine oligomers,[12] etc., apart from peptidomimetic foldamers.[13] Meijer and co-workers showed that even supramolecular polymers, formed by multiple H-bonds, could adopt a helical superstructure by specific noncovalent interactions between the monomeric units.[14] In most of these systems, the chain adopts a specific conformation primarily due to hydrogen bonding, steric and/or bond angle constraints and solvophobic effects. Metal-ion coordination of backbone heteroatoms in specifically designed oligomers has also been shown to generate folded structures in solution.[15]

Most of the above examples deal primarily with well-defined oligomers. Although several examples of high molecular weight polymers that adopt helical conformations in solutions are known, such as poly(trityl methacrylate)s,[16] polyisocyanates,[17] *cis*-poly(acetylene)s,[18] polyisocyanides,[19] and poly(1,3-phenylene ethynylene)s,[20] most of these deal with relatively stiff chains that

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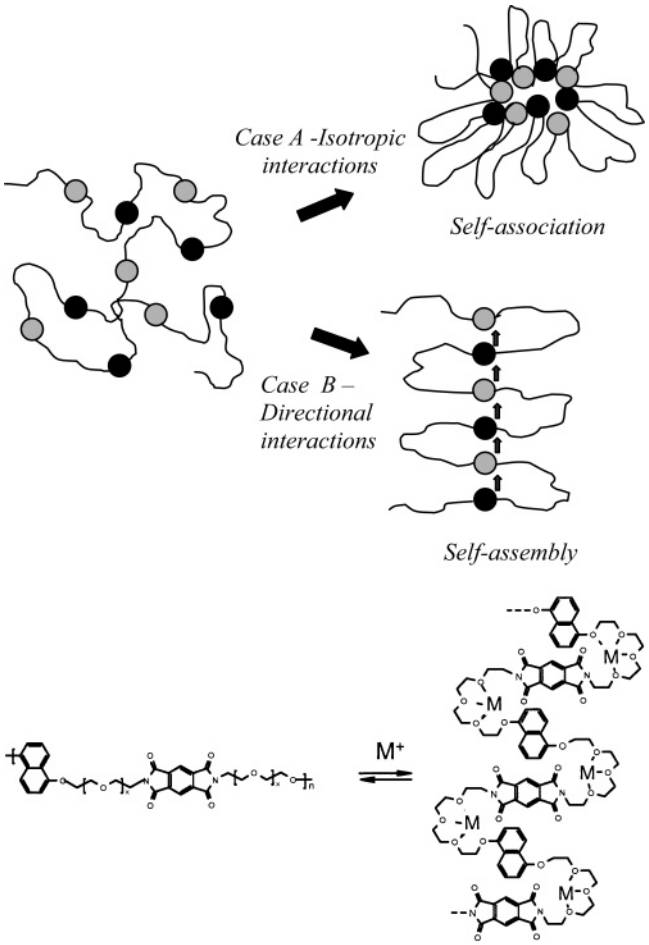
Scheme 1. Schematic Representation of the Principles for Folding, along with Our Design for a Foldamer



possess very limited conformational degrees of freedom due to the imposition of steric and/or bond-angle constraints. There are only very few examples wherein relatively flexible systems have been made to adopt a well-defined conformation in solution. One simple conceptual design for folding of flexible synthetic macromolecules can be schematically represented as shown in Scheme 1, wherein the polymer backbone is constituted of equi-spaced segments linked by flexible spacers. If such a polymer, for instance, is designed so that the flexible spacers are hydrophilic and the equi-spaced segments are hydrophobic, then in a polar medium the hydrophobic segments might be expected to cluster together (case A) in a process that could be termed as *intramolecular self-association*; a situation similar to micelle formation above the cmc.[21] If, on the other hand, an ordered *intramolecular self-assembly* has to occur, it is essential to ensure that the interaction between the equi-spaced segments is highly directional (case B). Thus, incorporation of highly directional interactions between equi-spaced segments along a flexible polymer chain could form a general basis of intrachain self-assembly or a directed folding process.

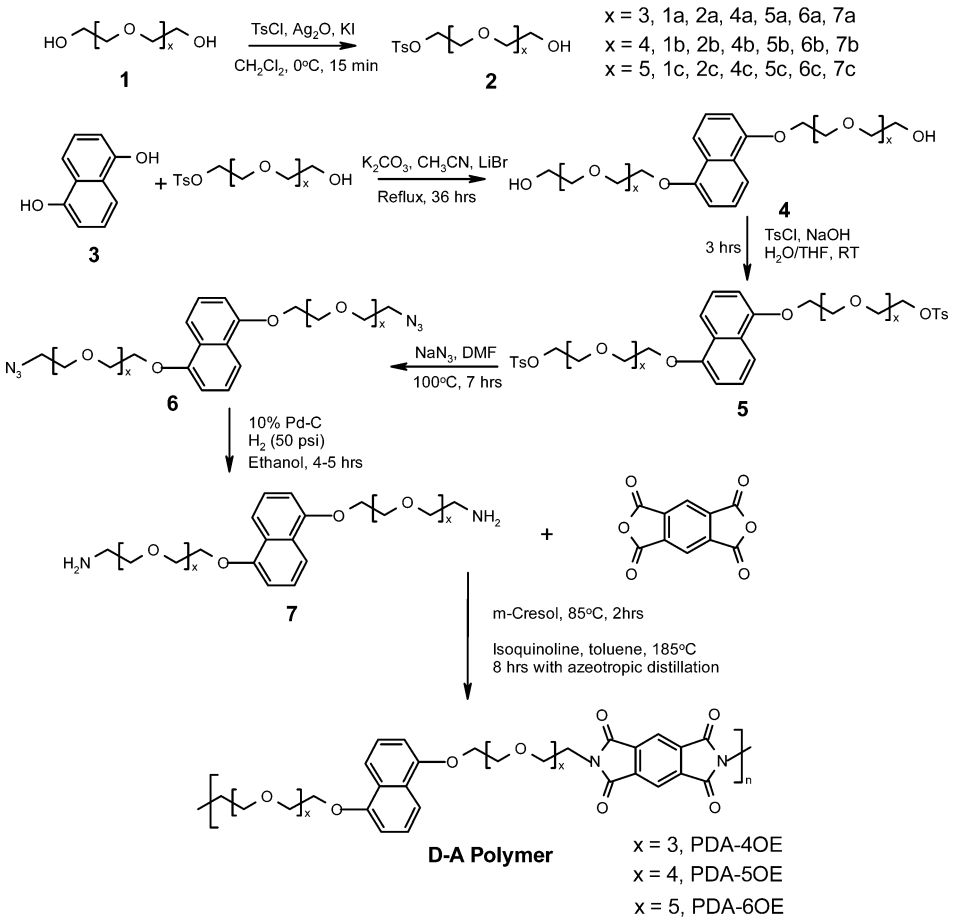
In line with these general principles, Iverson and co-workers described the folding of flexible oligomers in a series of elegant papers,[22] wherein they demonstrate the possibility of forming folded structures in suitably designed oligomers by virtue of specific intrachain aromatic donor−acceptor charge-transfer interactions (directional) aided by solvophobic effects. Similarly, Li and co-workers recently reported well-defined oligomers containing perylene units linked by oligo(oxyethylene) units and studied their folding properties (aided by directional π-stacking interactions).[23] Most of these studies on flexible foldamers have again dealt only with precisely defined oligomers, except for a recent report by Janssen and co-workers,[24] wherein the authors have postulated the formation of folded structures in polymers having perylene units separated by oligo(oxybutylene) units. In an effort to generate high molecular weight polymers that can fold via intramolecular self-assembly, we designed a polymer that contains 3-folding elements (see Scheme 1): (i) an alternate placement of aromatic donor and acceptor units that could form an intrachain donor−acceptor charge-transfer complex, analogous to the Iverson systems, (ii) a oligo(oxyethylene) (*n*OE) linking segment that could impart a solvophobic motivation for folding,[25] and (iii) the alkali-metal ion complexation ability of the flexible OE segment that could assist in the formation of folded structures by restricting the conformational freedom of the loop, which in turn could further aid the formation of the D−A charge transfer complex. Early comprehensive studies by Voglte and co-workers on podands clearly demonstrated the possibility of open chain analogues of crown ether to complex with metal ions and generate folded structures.[26] Several workers have exploited such metal-ion induced folding to modulate the photophysical properties in small molecules,[27] and very recently in polymers.[28] Similarly, D−A charge-transfer interactions have also been used to generate supramolecular systems as well as to modulate the conformations in small molecular systems.[29]

On the basis of the above design elements, in a preliminary study, we reported the synthesis and folding properties of a D−A polyimide, **PDA—6OE** (see Scheme 2), having a hexa(oxyethylene) linker segment.[30] The UV−visible and NMR spectroscopic studies as a function of solvent composition, and in the presence of varying amounts of alkali-metal ions, provided evidence in support of the postulate that the three aforementioned weak interactions could indeed work in tandem to generate a folded structure. In this paper, we examine the folding process in such (−donor−*spacer*−acceptor−*spacer*−)$_n$ type polymers, as a function of the length of the OE spacer in the nascent form as well as in the presence of different alkali-metal ions. Furthermore, we also present variable temperature spectroscopic studies that reveal the synergistic effects of the solvophobic interactions and metal-ion complexation on the folding process. Studies on specifically designed model compounds of the type donor−*spacer*−acceptor (DA), donor−*spacer*−acceptor−*spacer*−donor (DAD), and acceptor−*spacer*−donor−*spacer*−acceptor (ADA) are also presented, which further endorse the hypothesis that extended D−A stacking is present in the folded structures of the polymers.

Experimental Section

General Data. All the reagents and solvents were purified according to the prescribed procedure.[31] 1,5-Dihydroxynaphthalene and pyromellitic dianhydride (Aldrich Chemical Co.) were purified by recrystallization from nitromethane and acetic anhydride, respectively, and the latter was further vacuum sublimed. Tetraethylene glycol and *p*-toluene sulfonyl chloride were purchased from Aldrich Chemical Co. and used as such. Pentaethylene glycol (**1b**) and hexaethylene glycol (**1c**) were prepared following a literature procedure.[32] All the NMR

Scheme 2. Synthetic Scheme for the Preparation of the PDA−*n*OE Polymers



spectra were recorded in a Bruker 400 MHz NMR spectrometer, and the absorption spectra were recorder using a Hitachi U3400 spectrometer. The molecular weights were determined by GPC using chloroform as the eluent at 30 °C, two PLgel Mixed bed columns to effect separation and a Viscotek TDA, model 300, as the detector. The universal calibration method based on PS standards was used to estimate the molecular weights. The variable temperature UV−visible experiments were carried out using a Ocean Optics, SD2000 fiber optic-based spectrometer that utilized a homebuilt dry N_2 purged chamber, along with a refrigerated circulatory setup.

Monomer Synthesis. Compound 2a. Tetraethylene glycol (4 g, 0.021 mol) was dissolved in 100 mL of dry dichloromethane, and the solution was cooled to 0 °C. To this were added 7.2 g (0.031 mol) of freshly prepared Ag_2O, 4.33 g (0.022 mol) of *p*-toluene sulfonyl chloride, and 0.66 g of KI, and the resulting heterogeneous reaction mixture was stirred at 0 °C for another 15 min. The reaction mixture was filtered through a bed of silica gel, washed with ethyl acetate (3 × 10 mL), and the combined filtrate was concentrated to get a light yellow colored oil. The crude product was purified by column chromatography on silica gel column using chloroform/ethyl acetate as the eluent. The pure product was obtained as a colorless oil in 65% yield. **2b** and **2c** were prepared using the same procedure. Yields: **2b**, 70%; **2c**, 67%.

^{1}H NMR (400 MHz, $CDCl_3$): compound **2a**, δ (ppm) = 7.80 (d, 2H, Ar−*H*, *o*-SO_3−), 7.33 (d, 2H, Ar−*H*, *m*-SO_3−), 4.15 (t, 2H, −SO_2OCH_2−), 3.71−3.58 (m, 14H, oligoethylene *H*'s), 2.44 (s, 3H, Ar−CH_3); compound **2b**, δ (ppm) = 7.81 (d, 2H, Ar-*H,* *o*-SO_3−), 7.45 (d, 2H, Ar−*H*, *m*-SO_3−), 4.16 (t, 2H, −SO_2OCH_2), 3.73−3.59 (m, 18H, oligoethylene *H*'s), 2.45 (s, 3H, Ar−CH_3); compound **2c**, δ (ppm) = 7.72 (d, 2H, Ar−*H*, *o*-SO_3−), 7.27 (d, 2H, Ar−*H,* *m*-SO_3−), 4.09 (t, 2H, −SO_2OCH_2), 3.66−3.51 (m, 22H, oligoethylene *H*'s), 2.37 (s, 3H, Ar−CH_3).

Compound 4a. To a degassed solution of 1,5-dihydroxynaphthalene (1.33 g, 8.31 mmol) in dry acetonitrile (50 mL) were added compound **2a** (5.78 g, 16.6 mmol), anhydrous K_2CO_3 (4.53 g, 32.8 mmol), and a catalytic amount of LiBr, and the resulting reaction mixture was stirred under reflux condition for 36 h under a nitrogen balloon. After completion of the reaction, the contents were filtered, the residue was washed with acetonitrile several times, and the combined filtrate was concentrated. It was redissolved in 50-mL of dichloromethane and washed with a (3 × 50 mL) 3:1 mixture of brine and 10% NaOH solution. The organic layer was dried over Na_2SO_4 and concentrated to get a brown color oil as the crude product, which was used for the next step without further purification. Yield = 90%. **4b** and **4c** were prepared using a similar procedure from compound **2b** and **2c** in 80 and 92% yields**,** respectively.

Compound 5a. Compound **4a** (3.7 g, 7.24 mmol) was dissolved in 10 mL of THF and to this was added an aqueous NaOH solution (0.864 g in 6.5 mL of distilled water). The resulting mixture was cooled to 0 °C, and a solution of TsCl (3.11 g in 25 mL of dry THF) was added dropwise over a period of 30 min, keeping the temperature of the reaction mixture beween 0 and 5 °C. After the addition was completed, the reaction mixture was stirred at room temperature for 3 h, and the contents were poured into 60 mL of ice-cold water and extracted with dichloromethane (3 × 30 mL). The combined organic layer was washed with water and brine, dried with Na_2SO_4, and concentrated to get a brown colored oil as the crude product. It was purified over silica gel column using a mixture of chloroform/ethyl acetate as the eluent. Yield = 50%. A similar procedure was followed to make the compounds **5b** and **5c** starting from **4b** and **4c**, respectively. Yields: **5b** = 45%; **5c** = 54%.

^{1}H NMR (400 MHz, $CDCl_3$): compound **5a**. δ (ppm) = 7.831 (d, 2H, Ar−*H*, *p*-OCH_2), 7.770 (d, 4H, Ar−*H,* *o*-SO_3), 7.352−7.293 (m, 6H, Ar−*H*, *m*-OCH_2 and Ar−*H*, *m*-SO_3), 6.827 (d, 2H, Ar−*H*, *o*-OCH_2) 4.280 (t, 4H, Ar−O−CH_2), 4.118 (t, 4H, SO_2O-CH_2), 3.978 (t, 4H, Ar−O−CH_2CH_2O−), 3.772 (t, 4H,

Ar−O−$CH_2CH_2OCH_2$), 3.667−3.544 (m, 16H, rest of the oligooxyethylene *H*'s), 2.41 (s, 6H, Ar−CH_3); compound **5b**, δ (ppm) = 7.850 (d, 2H, Ar−*H*, *p*-OCH_2), 7.789 (d, 4H, Ar−*H*, *o*-SO_3,), 7.358−7.312 (m, 6H, Ar−*H*, *m*-OCH_2 and Ar−*H*, *m*-SO_3), 6.840 (d, 2H, Ar−*H*, *o*-OCH_2) 4.292 (t, 4H, Ar−O−CH_2), 4.137 (t, 4H, SO_2O-CH_2), 3.995 (t, 4H, Ar−O−CH_2CH_2O−), 3.800 (t, 4H, Ar−O−$CH_2CH_2OCH_2$), 3.706−3.560 (m, 24H, rest of the oligoethylene *H*'s), 2.429 (s, 6H, Ar−CH_3); compound **5c**, δ (ppm) = 7.84 (d, 2H, Ar−*H*, *p*-OCH_2), 7.78 (d, 4H, Ar−*H*, *o*-SO_3,), 7.32−7.25 (m, 6H, Ar−*H*, *m*-OCH_2 and Ar−*H*, *m*-SO_3), 6.825 (d, 2H, Ar−*H*, *o*-OCH_2) 4.279(t, 4H, Ar−O−CH_2), 4.13 (t, 4H, SO_2O-CH_2), 3.984 (t, 4H, Ar−O−CH_2CH_2O−), 3.790(t, 4H, Ar−O−$CH_2CH_2OCH_2$), 3.698−3.549(m, 32H, rest of the oligooxyethylene *H*'s), 2.42 (s, 6H, Ar−CH_3).

Compound 6a. Compound **5a** (2.42 g, 2.9 mmol) was dissolved in 20 mL of dry DMF, 2 g of NaN_3 (30 mmol) was added to it, and the contents were stirred at 100 °C for 7 h. The contents were cooled to room temperature and poured into 25 mL of ice-cold water. The product was extracted with diethyl ether (3 × 25 mL), and the combined ether layer was concentrated to obtain the crude product as a light yellow color oil. The product was obtained as a light yellow oil after purification on a silica gel column using a mixture of chloroform and ethyl acetate as the eluent. Yield: 75%. Compounds **6b** and **6c** were prepared following a similar procedure starting from **5b** and **5c**, respectively. Yields: **6b** = 70%; **6c** = 72%.

^{1}H NMR (400 MHz, $CDCl_3$): compound **6a**, δ (ppm) = 7.852 (d, 2H, Ar−*H*, *p*-OCH_2), 7.337 (t, 2H, Ar−*H*, *m*-OCH_2), 6.834 (d, 2H, Ar−*H*, *o*-OCH_2), 4.290 (t, 4H, Ar−OCH_2), 3.981 (t, 4H, Ar−OCH_2CH_2), 3.798 (t, 4H, Ar−$OCH_2CH_2OCH_2$−), 3.343 (t, 4H, N_3-CH_2), 3.717−3.627 (m, 16 H, rest of the oligooxyethylene *H*'s); compound **6b**, δ (ppm) = 7.860 (d, 2H, Ar−*H*, *p*-OCH_2), 7.347 (t, 2H, Ar−*H*, *m*-OCH_2), 6.841 (d, 2H, Ar−*H*, *o*-OCH_2), 4.297 (t, 4H, Ar−OCH_2), 4.002 (t, 4H, Ar−OCH_2CH_2), 3.811 (t, 4H, Ar−$OCH_2CH_2OCH_2$−), 3.365 (t, 4H, N_3-CH_2), 3.720−3.633 (m, 24 H, rest of the oligooxyethylene *H*'s); compound **6c**, δ (ppm) = 7.846(d, 2H, Ar−*H*, *p*-OCH_2), 7.33 (t, 2H, Ar−*H*, *m*-OCH_2), 6.83 (d, 2H, Ar−*H*, *o*-OCH_2), 4.284 (t, 4H, Ar−OCH_2), 3.989(t, 4H, Ar−OCH_2CH_2), 3.797 (t, 4H, Ar−$OCH_2CH_2OCH_2$−), 3.361(t, 4H, N_3-CH_2), 3.705−3.634 (m, 32 H, rest of the oligooxyethylene *H*'s).

Compound 7a. 6a (1.2 g, 2.13 mmol) was dissolved in 10 mL of ethanol, and to this solution was added 80 mg of 10% Pd−C. The reaction mixture was mechanically stirred under 50 psi of H_2 pressure for 5 h, with intermittent recharging with fresh hydrogen gas. After 5 h, the reaction was stopped and the contents were filtered under suction. The filtrate was concentrated to give a green color oil, which was purified on a neutral alumina column (under a N_2 atmosphere), using 2% methanol in chloroform as the eluent, to get the pure diamine monomer in 90% yield. Similarly, compounds **7b** and **7c** were obtained starting from **6b** and **6c**, respectively. Yields: **7b** = 88% and **7c** = 85%.

^{1}H NMR (400 MHz, $CDCl_3$): compound **7a**, δ (ppm) = 7.860 (d, 2H, Ar−*H*, *p*-OCH_2), 7.346 (t, 2H, Ar−*H*, *m*-OCH_2), 6.843-(d, 2H, Ar−*H*, *o*-OCH_2), 4.302 (t, 4H, Ar−OCH_2), 4.001 (t, 4H, Ar−OCH_2CH_2), 3.710 (t, 4H, Ar−$OCH_2CH_2OCH_2$−), 3.483 (t, 4H, NH_2CH_2), 2.835 (t, 4H, NH_2), 3.726−3.465 (m, 16 H, rest of the oligooxyethylene *H*'s); compound **7b**, δ (ppm) = 7.859 (d, 2H, Ar−*H*, *p*-OCH_2), 7.347 (t, 2H, Ar−*H*, *m*-OCH_2), 6.845 (d, 2H, Ar−*H*, *o*-OCH_2), 4.298 (t, 4H, Ar−OCH_2), 4.000 (t, 4H, Ar−OCH_2CH_2), 3.820 (t, 4H, Ar−$OCH_2CH_2OCH_2$−), 3.483 (t, 4H, NH_2CH_2), 2.832 (t, 4H, NH_2), 3.717−3.457 (m, 24 H, rest of the oligooxyethylene *H*'s); compound **7c**, δ (ppm) = 7.84 (d, 2H, Ar−*H*, *p*-OCH_2), 7.33 (t, 2H, Ar−*H*, *m*-OCH_2), 6.83 (d, 2H, Ar−*H*, *o*-OCH_2), 4.285 (t, 4H, Ar−OCH_2), 3.988 (t, 4H, Ar−OCH_2CH_2), 3.797 (t, 4H, Ar−$OCH_2CH_2OCH_2$−), 3.473 (t, 4H, NH_2CH_2), 2.835 (t, 4H, NH_2), 3.7−3.6 (m, 32 H, rest of the oligooxyethylene *H*'s).

PDA—4OE. Diamine **7a** (0.496 g, 0.971 mmol) was dissolved in 3 mL of distilled *m*-cresol, and to this stirred solution was added pyromellitic dianhydride (0.211 g, 0.971 mmol). The flask was then immersed into a preheated (80 °C) oil bath, and the contents were stirred under N_2 atmosphere for 2 h. After cooling to room temperature, 4.2 mL of dry toluene, containing 7 drops of isoquinoline, was added to it, and the temperature was gradually raised to 185 °C. The reaction mixture was stirred at 185 °C for 7 h with continuous removal of the water generated as a water/toluene azeotrope. The deep red-colored viscous solution was poured into methanol to obtain the polymer as orange colored fibrous precipitate. The polymer was purified by fractionation using chloroform/methanol. Yield = 69%. **PDA—5OE** and **PDA—6OE** were prepared by the same procedure. Yields: **PDA—5OE** = 60% and **PDA—6OE** = 63%. ^{1}H NMR (400 MHz, $CDCl_3$) for **PDA—4OE**, δ (ppm) = 7.830 (s, 2H, imide ring *H*'s) 7.574 (d, 2H, Ar−*H*, *p*-OCH_2), 7.154 (t, 2H, Ar−*H*, *m*-OCH_2), 6.693 (d, 2H, Ar−*H*, *o*-OCH_2), 4.190 (t, 4H, Ar−OCH_2), 3.957 (t, 4H, Ar−OCH_2CH_2), 3.875 (t, 4H, N-CH_2) 3.764 (t, 4H, Ar−OCH_2CH_2-OCH_2−), 3.661 (broad peak, 16H, rest of the oligooxyethylene *H*'s).

^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) = 166.10, 154.15, 136.42, 126.32, 125.13, 117.25, 114.31, 105.54, 71.14, 70.78, 70.65, 70.29, 69.77, 67.81, and 37.93.

PDA—5OE. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.059 (s, 2H, imide ring *H*'s) 7.712 (d, 2H, Ar−*H*, *p*-OCH_2), 7.250 (merged with the chloroform peak in $CDCl_3$. 2H, Ar−*H*, *m*-OCH_2), 6.765 (d, 2H, Ar−*H*, *o*-OCH_2), 4.245 (t, 4H, Ar−OCH_2), 3.973 (t, 4H, Ar−OCH_2CH_2), 3.895 (t, 4H, N-CH_2) 3.793−3.605 (m, 28H, Ar−$OCH_2CH_2OCH_2$− and the rest of the oligoethylene *H*'s).

^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) = 166.15, 154.21, 136.76, 126.48, 125.12, 117.19, 114.49, 105.59, 71.00, 70.63, 70.05, 69.80, 67.79, and 37.84.

PDA—6OE. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.073 (s, 2H, imide ring *H*'s) 7.71 (d, 2H, Ar−*H*, *p*-OCH_2), 7.24 (t, 2H, Ar−*H*, *m*-OCH_2), 6.75 (d, 2H, Ar−*H*, *o*-OCH_2), 4.247 (t, 4H, Ar−OCH_2), 3.976 (t, 4H, Ar−OCH_2CH_2), 3.903 (t, 4H, N−CH_2) 3.794 (t, 4H, Ar−$OCH_2CH_2OCH_2$−), 3.756−3.529 (m, 32H, rest of the oligoethylene *H*'s).

^{13}C NMR (400 MHz, $CDCl_3$):166.16, 154.20, 136.7, 126.50, 125.08, 125.08, 117.55, 114.50, 105.60, 70.99−69.80, 67.83, 67.73, 37.85.

Fractionation of the PDA—*n*OE polymers. In a typical fractionation procedure, 100 mg of the polymer was dissolved in 7−8 mL of chloroform and then methanol was added dropwise to this orange color solution until it became cloudy. It was then stirred for 10−15 min and centrifuged. The supernatant was decanted and the residue was dissolved in minimum quantity of chloroform and reprecipitated from methanol to get the high molecular weight fraction. The polymers were dried under vacuum at 100 °C for 5−6 h. The fractionated polymer was typically obtained in 20−25% with respect to the nascent polymer taken.

Synthesis of the Model Compounds. Compounds **7a** and **7b** have been used for making **ADA—4OE** and **ADA—5OE**, respectively. However, unlike during polymerization, here the pyromellitic dianhydride was taken in excess, and the terminal anhydride units were capped by reacting with excess *n*-propylamine. The required compound was obtained by column chromatography using silica gel as stationary phase and mixture of chloroform/ethyl acetate as the eluent. For DA and DAD type model compounds, the amine-containing donor units were first prepared (as for the polymers) from 5-methoxynaphthol instead of 1,5-hydroxynaphthalene. The monoamine was coupled with pyromellitic dianhydride, along with *n*-propylamine (in a 1:1:1 mole ratio) leading to a mixture of DAD, DA, and simple A-type compounds. The required DAD- and DA-type models were separated by column chromatography using silica gel as the stationary phase and chloroform/ethyl acetate mixture as eluent. Further details of the experimental procedure for the various model compound synthesis, along with their spectral data, can be found in the Supporting Information.

Folding Studies. The alkali-metal salts were purified by recrystallization, and the solvents $CDCl_3$ and CH_3CN were dried before use. For NMR complexation studies, 1.5 mL of the polymer/model compound solution was prepared in 1:1 $CDCl_3/CH_3CN$ (concentration range: 1−3 mM) (solution **A**). To 0.9 mL of solution **A**, a calculated amount of the appropriate

Table 1. Yield and Molecular Weights of the DA Polymers

polymer	yield (%)	M_n (PDI)[a]
PDA—4OE	69	43300 (2.1)
PDA—5OE	60	30000 (2.2)
PDA—6OE	63	49600 (2.0)

[a] Molecular weights of the fractionated samples determined by GPC.

alkali-metal salt (~10−15 molar equivalents with respect to one oligooxyethylene segment) was added (solution **B**). 0.6 mL of solution **A** was then taken in an NMR tube, and to it was added solution **B** in 20−100 μL steps. This resulted in a series of solutions having a fixed polymer/model compound concentration but varying amounts of the alkali-metal salts. The δ values in all the proton NMR studies are referenced with respect to TMS. The UV−visible studies were also carried out in a similar manner maintaining a fixed polymer/model compound concentration of 1 mM, in the same solvent mixture.

Results and Discussion

Synthesis and Characterization. The synthesis of the DA polyimides, **PDA—*n*OE**, was carried out as per Scheme 2. In essence, 1,5-dihydroxynaphthalene was first alkylated using the appropriate oligoethylene glycol monotosylate,[33] followed by tosylation of the terminal hydroxyl groups in the coupled product, and subsequent transformation of the tosylates to amines in two steps via an azide intermediate. The diamine containing the donor naphthalene unit (**7**) is then condensed with pyromellitic dianydride under standard polyimide synthesis conditions to generate the DA polymers.[34]

Wholly aromatic polyimides typically have very poor solubility, however, the present samples with flexible spacers are readily soluble in chloroform.[35] Three different polymers with varying lengths of the OE segments, **PDA—4OE**, **PDA—5OE**, and **PDA—6OE** were synthesized and characterized by ^{1}H and ^{13}C NMR to confirm their structure.[36] The molecular weights (M_n) of the nascent polymers were in the range 15000−20000, which after fractionation increased to 30000−50000 (see Table 1).[37] All the folding studies were carried out with the high molecular weight fractionated samples to ensure that the observed effects represent the behavior of true polymers.[38]

Penta- and hexa(ethylene glycols) were synthesized from the smaller glycols according to reported procedures.[32] All the polymers formed intensely red-colored elastic films upon solvent casting due to the presence of strong charge-transfer interactions in the solid state. Analogous OE spacers containing polyimides,[39] which do not contain the donor naphthalene units, on the other hand, are white, confirming that the color is indeed due to the CT complex formation.

The aromatic region of the ^{1}H NMR spectra of the three **PDA—*n*OE** samples is shown in Figure 1, along with the peak assignments.[40] One striking observation when comparing these spectra is the relative position of the aromatic signals, in particular the single peak (Ha) corresponding to the pyromellitic−diimide unit, which in the case of **PDA—4OE** is considerable upfield shifted when compared to the other two polymers. In all cases, note that all the aromatic peaks are upfield shifted compared to those in a 1:1 mixture of the model donor (D) and acceptor (A) molecules (see Scheme 3 for their structures). As discussed in our earlier paper,[30] such an upfield shift can be ascribed to the formation of a D−A charge-transfer complex. On the basis of the magnitude of the upfield shift, one can conclude that the extent of such C−T intrachain interactions among the nascent polymers (in a good solvent, like chloroform) is highest in the case of **PDA—4OE** and is lesser in the other two cases.[41]

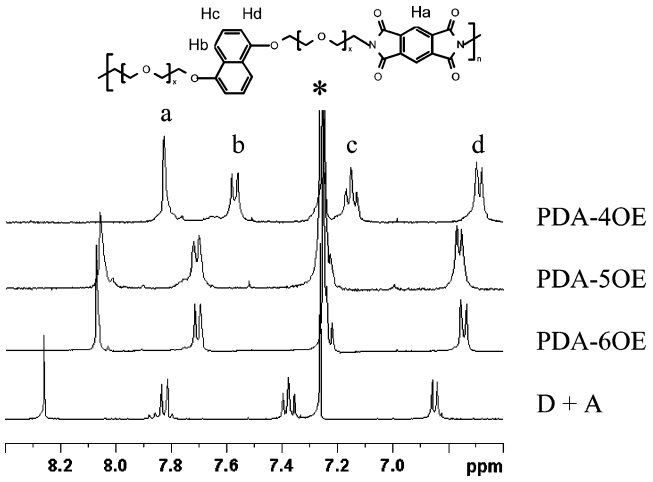
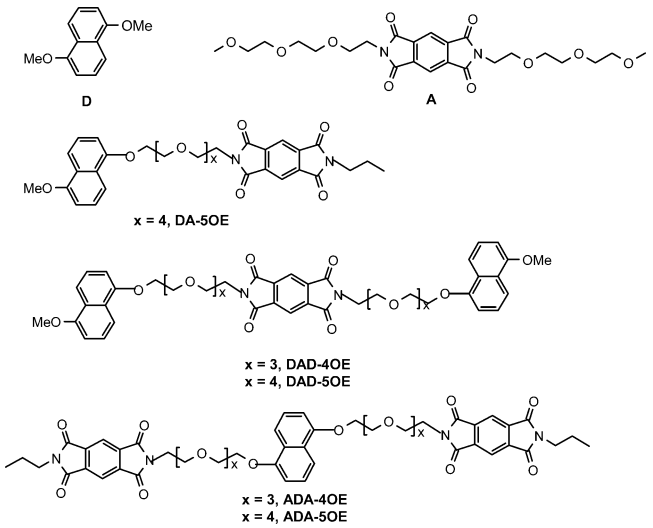


Figure 1. Comparison of ^{1}H NMR spectra (aromatic region) of the various polymers with the mixture of (D + A) model compounds (in $CDCl_3$). The peak marked by an asterisk is due to solvent.

Scheme 3. Structure of Various Model Compounds



Similarly, the relative absorbances of the charge-transfer band in the UV−visible spectra of the three polymers (see Figure 2) reveal the greater propensity for **PDA—4OE** to form folded structures. Here again, it is clear that linking of the donor and acceptor units periodically along the polymer chain causes a significant increase in the extent of CT interaction (compare the absorbances in the polymers with that in the D + A mixture). To ensure that the interactions in the polymers are indeed intrachain, dilution studies (in the range 0.75−0.06 mM) were done, and it was shown that the CT band intensity follows the expected Beer−Lambert behavior (see inset in Figure 2).

Variable Temperature Studies. Folding of polymers to generate well-defined secondary structures being an entropically disfavored process is expected to exhibit fairly strong temperature dependence. To examine this, we first carried out variable temperature ^{1}H NMR studies of all the three DA polyimides in a good solvent, like chloroform. The NMR stack plot of these

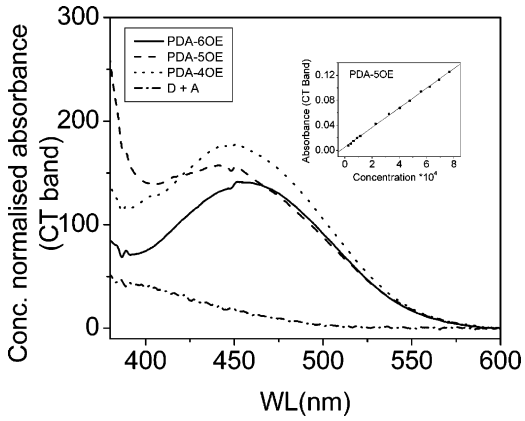


Figure 2. Comparison of UV−visible spectra (CT region alone) of the various polymers in chloroform, along with that of a mixture of model compounds. Inset: Variation of A_{CT} with concentration for **PDA—5OE** in $CHCl_3$.

studies for **PDA—4OE** and **PDA—6OE** is shown in Figure 3.

It is seen that there is considerable upfield shift of the aromatic proton signals with decreasing temperature in the case of **PDA—4OE**, while the shift is minimal in the case of **PDA—6OE**. A plot of the variation in the chemical shift of the acceptor aromatic protons in the three different polymers as a function of temperature is shown in Figure 4b. It is clear from this plot that the change in δ value is significant only in the case of **PDA—4OE**, while it is marginal in the other two polymers. In contrast, however, all the three polymers exhibit a continuous increase in the CT-band intensity with decreasing temperature (Figure 4a). This difference in the temperature dependences of the NMR and UV−visible spectra appears to reflect the different sensitivities of the two techniques to the folding process; the NMR chemical shifts appear to be very sensitive to the formation of extended stacks, which causes the acceptor units to be sandwiched between two adjacent donors and vice versa, while the absorbance of the CT-band appears to primarily sense only the number of D−A contacts induced upon folding.[42]

To gain further understanding of the folding process, three types of model compounds, namely, donor−*spacer*−acceptor (DA) and analogous DAD and ADA (Scheme 3), were synthesized and characterized by standard techniques.[40] In Figure 5, we compare the proton NMR spectra of the two model compounds having a tetra(oxyethylene) spacer (4OE), along with that of the corresponding polymer **PDA—4OE** and a 1:1 mixture of D and A model compounds.

A few important observations regarding the relative positions of the aromatic protons in these systems can be made: (a) the chemical shift of acceptor proton of the polymer lies close to that of model DAD, while that of the model ADA is considerably downfield shifted; (b) the chemical shift of donor protons (Hb shown in Figure 1) in ADA lies very close to that in the polymer, while that of the model DAD appears downfield. These observations confirm that the chemical shift of the aromatic protons are sensitive at one level to the formation of a simple DA pair (as evident from the upfield shift of both D and A protons in all model compounds when compared to those in the D + A mixture), while the formation of a sandwiched structure, wherein either the acceptor lies between two donors (or vice versa), causes a further significant upfield shift. It is also observed that, in all cases, the acceptor protons appear to be intrinsically more sensitive to stacking than the donor protons for reasons that are still unclear. The greater tendency for the polymer with the shorter spacer (**PDA—4OE**) to form folded structures is also clearly reflected in the temperature dependence of the NMR spectra of the model DAD model systems containing different OE spacers (see Figure 6); the acceptor proton in **DAD—4OE** exhibits a very large upfield shift causing it to move past the donor protons (Hb), while the corresponding peak in **DAD—5OE** shifts very little.

If we consider the fully folded and unfolded states to be in equilibrium via an intermediate state wherein only D−A contacts are established (as depicted in Scheme 4), it is apparent from the foregone discussions that the folded form is relatively more stable in the case of **PDA—4OE** than in the other two cases.[43] While cooling appears to cause an increase in the extent of CT complex formation in all cases (based on UV−visible spectral changes), in the case of **PDA—4OE**, it also results in the formation of an extended array of alternately

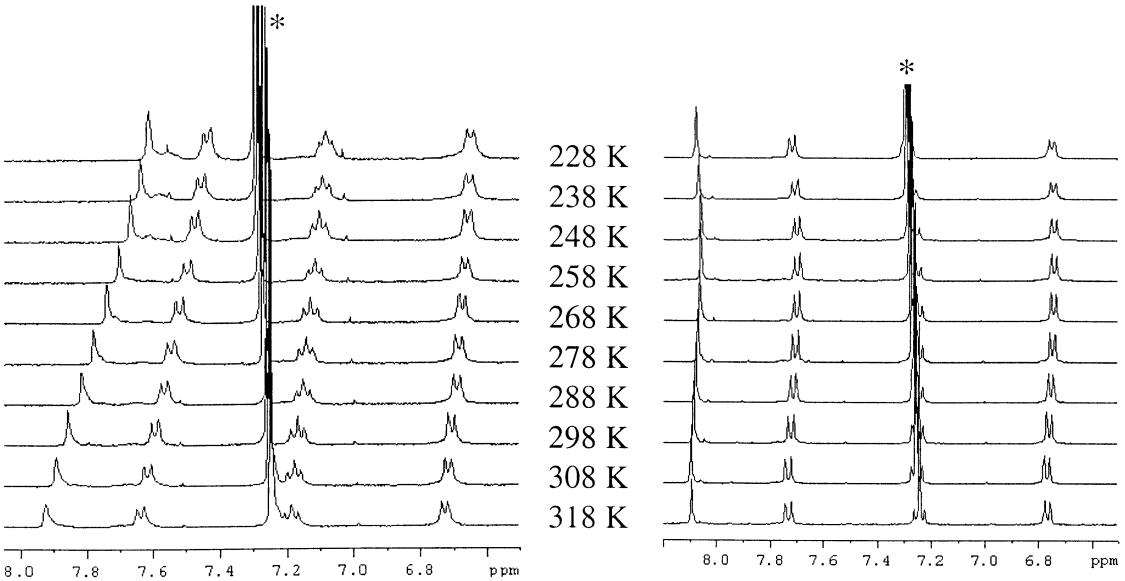


Figure 3. Variation of ^1H NMR spectra of **PDA—4OE** (left) and **PDA—6OE** (right) as a function of temperature (in $CDCl_3$). (*) due to solvent.

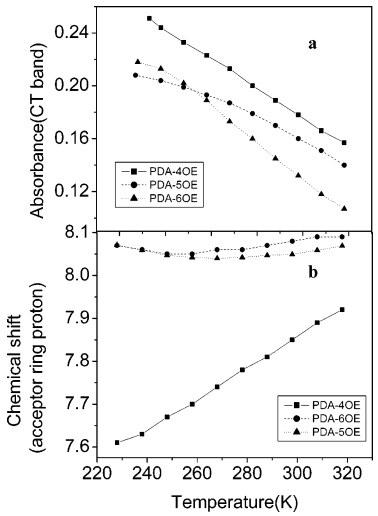


Figure 4. Variation of A_{CT} (a, top) (in chloroform at 1 mM) and δ value of acceptor proton (b, bottom) of the various polymers as a function of temperature (in $CDCl_3$).

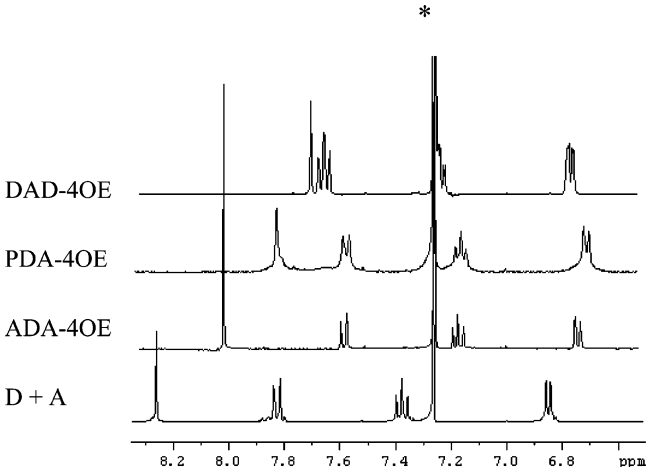
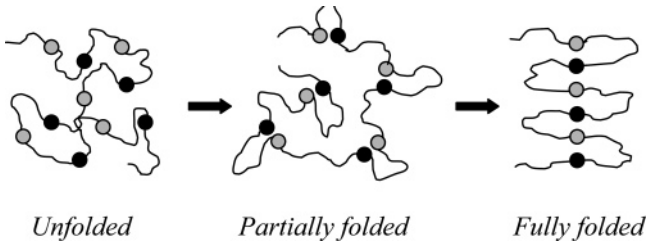


Figure 5. Comparison of ^1H NMR spectra (aromatic region) of polymer **PDA—4OE** with the analogous model compounds, along with that of the mixture of (D +A) model compounds (in $CDCl_3$). (*) due to solvent.

Scheme 4. Schematic Depiction of the Evolution of the Folded Structure in the Polymer



stacked D and A units (extended folded state), as evident from the significantly larger shift of the acceptor proton peaks in its NMR spectra upon cooling (see Figure 4). These observations, in turn, suggest that increasing the stability of the folded state (externally) in either **PDA—5OE** or **PDA—6OE** should also result in a similarly enhanced temperature dependence of their folding process. It was shown in our earlier paper that the formation of the folded state in **PDA—6OE** could be significantly enhanced either by increasing the solvent polarity and/or by complexing the OE loop with a suitable alkali-metal ion.[30] In Figure 7, we compare the temperature dependence of the acceptor proton chemical shifts of nascent **PDA—6OE** with those in the presence of a polar solvent (40% (v/v) CD_3OD in $CDCl_3$) and in the presence of excess KSCN (9 equiv per repeat unit). The range over which the temperature dependence could be studied was slightly limited by either the precipitation of the polymer in the former case or due to the precipitation of the salt in the latter. However, it is apparent that the anticipated enhanced temperature dependence is realized when the folded state is stabilized either due to solvophobic interactions and/or due to complexation of the OE loop around the metal ion; the latter exhibits a stronger effect due to a combined effect of both the factors (studies carried out in 1:1 $CDCl_3/CH_3CN$) causing what appears to be extended stacking.[44]

Alkali-Metal Ion Complexation Studies. It is well-known that podands, as with their cyclic crown ethers analogues, exhibit an ionic size-dependent complexation with alkali-metals ions.[26] We studied this selectivity by examining the ability of various alkali-metal ions to enhance the formation of the folded structure in the polymers containing different OE spacers. The variation of CT band intensity as a function of varying alkali-metal ion concentration for all the polymers was examined; in the case of **PDA—4OE** no significant change in the absorption spectra was noticed even in the presence of the smallest Li ion, and therefore variation in the presence of the larger ions was not examined. The variation of the CT band intensity is plotted as a function of different metal-ion concentrations, for both **PDA—5OE** and **PDA—6OE** (see Figure 8). The OE spacer length-based selectivity is evident when one compares the changes that occur in the two cases; in **PDA—6OE**, K ion causes the maximum change followed by Na and Li, but in **PDA—5OE**, the effect of Li ion is largest followed by Na and K.[45]

The variation of the NMR spectra of both these polymers in the presence of various metal ions was similarly examined.[46] A plot of the variation of the chemical shift of the acceptor aromatic proton Ha (shown in Figure 1) as a function of metal-ion concentration (see Figure 8b) roughly parallels the changes observed in the CT band intensity,[47] thereby confirming the size-selective nature of the binding of the loop. Unlike in the variable temperature studies of nascent samples, here both the spectroscopic techniques exhibit significant and roughly similar changes, suggesting that the complexation of the loop by a metal ion aids extended stacking of the D and A units, thereby equally affecting their NMR spectra. In other words, the metal ion complexation of the OE spacers helps the polymer chain go from a partially folded state toward a fully folded one, as depicted in Scheme 4.

The metal-ion titration studies of the model compounds reveal similar selectivity pattern, while at the same time they also provide additional information that reflects on the nature of the CT complex formed and the extent of folding. To make a quantitative comparison of the variations, in Figure 9, we plot the changes in observed in the chemical shifts of the aromatic acceptor proton (Ha) and donor proton (Hb), in **PDA—5OE** and analogous models, as a function of metal-ion concentration. First, we observe that the chemical shift of the acceptor proton of the nascent polymer **PDA—5OE** lies very close to that of the corresponding **DAD—5OE** model. Furthermore, the variation of the δ values of the acceptor protons in the polymer, as a function of metal-

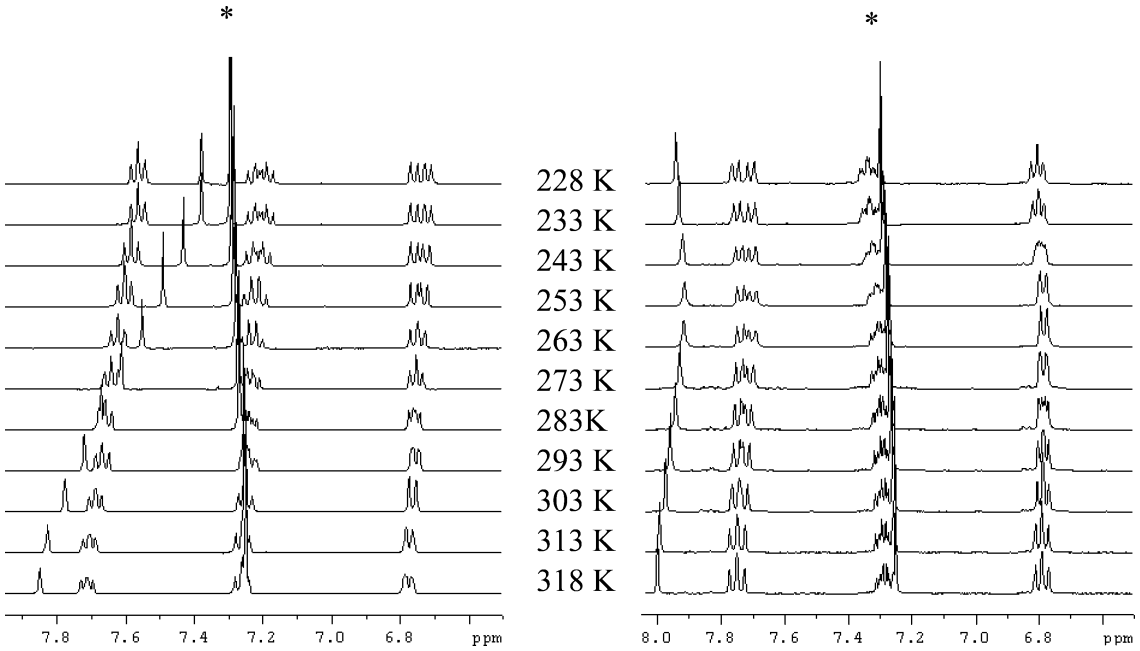


Figure 6. Variation of ^{1}H NMR spectra (aromatic region) of **DAD—4OE** (left) and **DAD—5OE** (right) as a function of temperature (in $CDCl_3$). (∗) due to solvent.

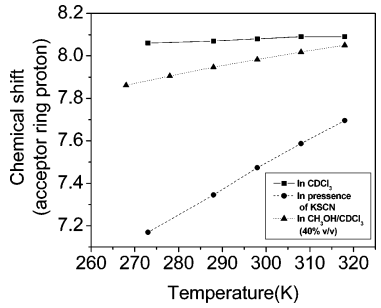


Figure 7. Variation of δ value of the acceptor proton of **PDA—6OE** as a function of temperature, under different conditions.

ion concentration, parallels that of the DAD model, while the corresponding variation in the case of the simple DA and ADA models is smaller and remain clustered together in the same chemical shift region. On the other hand, the variation of the δ values of the donor aromatic proton (Hb) in the ADA model and the polymer follows a similar pattern and fall in the same region, while those of the DA and DAD models vary to a smaller extent and in a parallel manner. These observations can be rationalized as follows: in DAD and DA models the donor can never be sandwiched, and likewise in ADA and DA the acceptor cannot be sandwiched. Therefore, the observation that the acceptor proton of polymer **PDA—5OE** behaves similar to that in the DAD model, while the donor proton mimics the changes seen in the ADA model, provides further evidence in support of the hypothesis that in the presence of a suitable alkali-metal ion (Li^+ for 5OE segment in the present example), the

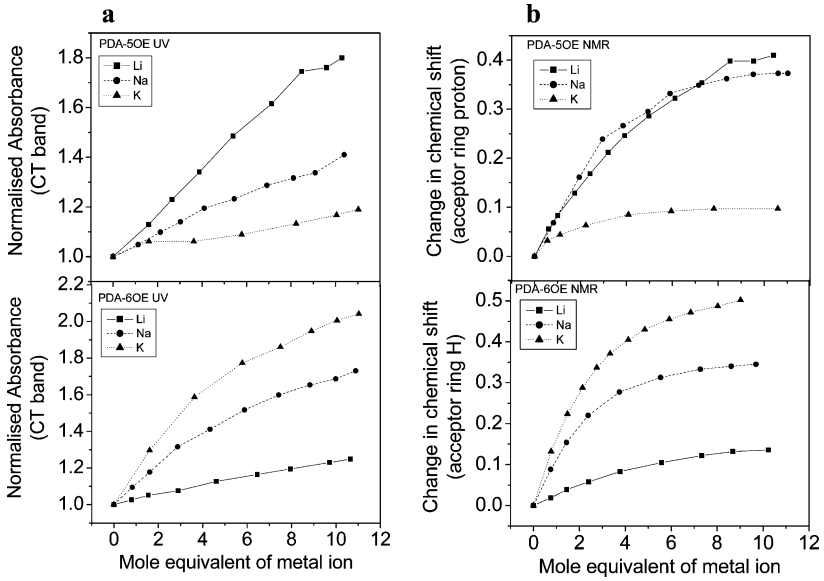


Figure 8. Variation of normalized A_{CT} (left) (in 1:1 chloroform−acetonitrile) of different polymers as a function of concentration of various alkali-metal ions, and the change of δ values of the acceptor proton (right) with concentration of alkali-metal ions (in 1:1 v/v $CDCl_3/CH_3CN$). Concentration of metal ions is taken with respect to polymer repeat unit; each repeat unit has two EO segments.

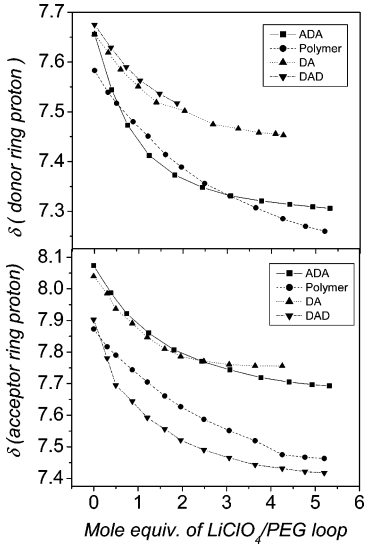


Figure 9. Variation of δ value of donor protons (top) and acceptor protons (bottom) of **PDA—5OE** and the analogous model compounds as a function of $LiClO_4$ concentration in 1:1 $CDCl_3/CH_3CN$. The donor peak of DAD merges with the solvent/acceptor peak and changes very little beyond 2 equiv of Li, and hence its δ value is not plotted beyond this point. (see Figure S16 in Supporting Information).

polymer folds to form extended stacks built up of alternating donor and acceptor units (approaching the fully folded state depicted in Scheme 4).[48]

One other intriguing observation that was made while studying the metal-ion titration of the **DAD—5OE** model compound is the large splitting of the peaks belonging to the naphthalene donor unit in the presence of Na, which is less apparent in the presence of Li (see Figure 10). To begin, each of the three pairs of aromatic protons belonging to the two rings in the naphthalene unit of **DAD—5OE** appear at near identical chemical shifts, although they are chemically nonequivalent. However, in the presence of increasing Na ion concentration this coincidental overlap is lifted causing one set of peaks to shift considerably upfield compared to the other (the most affected donor peaks are Ha′ and Hc′). Based on HMQC experiments, the peaks that shift more are assigned to the ring that has the methoxy substitutent, as shown in Figure 10.

We speculate that the origin for this lies in the exact geometry of the charge-transfer complex in **DAD—5OE**, which is significantly different in the case of the Na complex when compared to the Li one.[49] It appears that complexation of the flexible OE spacer with the larger size Na involves all the heteroatoms in the loop, while in the case of Li, the heteroatoms close to the D and A units are not directly involved. Because of this difference, the D and A units in the case of Li have greater freedom to adopt the most optimum geometry for effective CT complex formation. Two experimental observations support of this hypothesis: one is the significantly higher intensity of the CT band in the case of Li complex (which is accompanied by a red-shift of the λ_{max} that not seen in the case of Na complex), despite a lower value for the association constant (compared to Na) obtained from the NMR spectral variation (see Figure S28 in Supporting Information). The second relates to the changes that occur in the aliphatic region of the NMR spectra as a function of metal-ion concentration; it is seen that the methylene protons adjacent to the oxygen atom linked to the naphthalene unit shifts downfield in the case of the Na complex, while in the case of Li they shift very little (see Figure S29 in Supporting Information). This kind of splitting of the naphthalene protons in the presence of Na is seen only when the donor units cannot be sandwiched between two acceptors, as in the DA and DAD models, but no such splitting is seen in the case of the polymers and the ADA model compound.[50] Furthermore, inducing CT complexation by lowering the temperature also does not

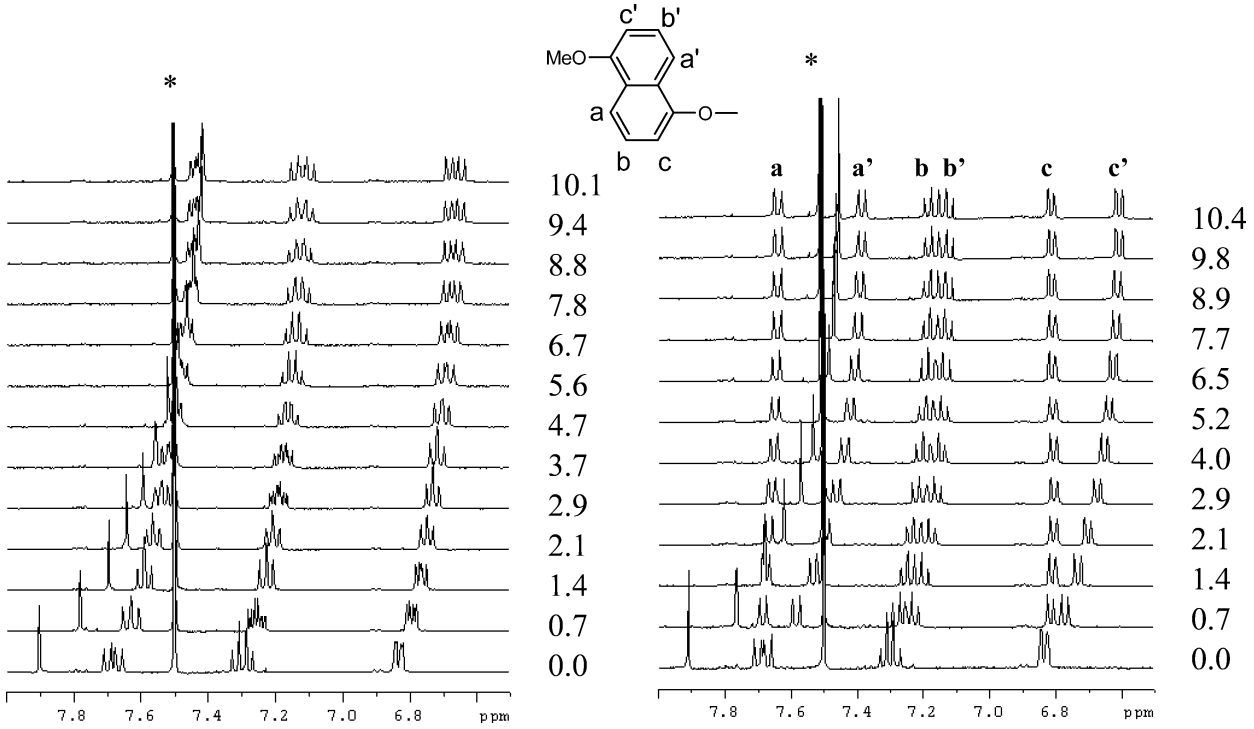


Figure 10. Variation of of ^1H NMR spectra (aromatic region) of **DAD—5OE** in 1:1 $CDCl_3/CH_3CN$ as a function of varying concentrations of $LiClO_4$ (left) and NaSCN (right). The numbers represent the mole ratio of the alkali-metal ion; (*) due to solvent.

induce any such splitting in the **DAD—4OE** (see Figure 6), suggesting that in the optimum geometry for effective charge-transfer, the two aromatic rings of naphthalene remain undifferentiated. Thus, in the case of Na complexation with **DAD—5OE**, the complexation of the OE loop dictates the relative positioning of the donor and acceptor, while Li complexation does not impose any such constraint.

Conclusions

In conclusion, a novel design for flexible high molecular weight polymers that are capable of intrachain self-assembly has been demonstrated. The design relies on periodic placement of aromatic units of opposite electron demand (donor and acceptor) along a polymer chain, wherein an oligo(oxyethylene) (*n*OE) linker serves both as a solvophobic motivator for folding and at the same time is also capable of complexation with alkali-metal ions thereby assisting the formation of a stacked array of D and A units. By varying the length of the OE spacer, it is shown that in the nascent form the polymer **PDA—4OE**, having a tetra(oxyethylene) unit, exhibits the highest propensity to form such folded structures. However, upon complexation of the OE spacer with alkali-metal ions of appropriate size the other polymers, **PDA—5OE** and **PDA—6OE**, also formed folded structures containing a similar alternately stacked array of D and A units. The selectivity of the OE spacers to ions of varying size is also clearly revealed by both the NMR titrations studies and analogous UV−visible studies. Comparison of the spectral changes seen in the polymers, as a function of temperature and upon metal ion complexation, with those in analogous model compounds, provide clear evidence for the formation of the postulated intrachain stacked D−A arrangement. Although the exact length scale over which such a stacking occurs remains a challenging problem to address,[51] it is evident that in the folded structure the acceptors are sandwiched between two donors and the donors between two acceptors; this is most pronounced in a polar medium containing an excess of the appropriate alkali-metal ion. It was also concluded that while the complexation of the OE spacer clearly enhances the charge-transfer interaction, it does not necessarily allow the optimum geometry for most effective CT interaction between the D and A units; larger ions, which indulge all the heteroatoms of the linker segment in the complexation, restricts the mobility of the D and A units leading to less effective interaction, while smaller ions allow greater conformational freedom for more effective CT interaction. In summary, we have demonstrated that by the use of several weak but directional intrachain intersegment interactions, suitably designed synthetic polymers can be coerced into adopting a specific folded conformation. Alternate designs for generating folded structures as well as newer methods to examine folding are currently being explored.

Acknowledgment. We would like to thank DST, MHRD, and 3M-India for their generous support.

Supporting Information Available: Text and schemes giving synthetic methods and characterization of all model compounds and figures showing complete spectral data (^{1}H and ^{13}C NMR) of all polymers, GPC chromatograms, and all spectral variations (not included in main text) of polymers and model compounds as a function of temperature and metal-ion concentration, and a table giving the apparent association constant of the polymers with various alkali-metal ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) The polymer **PDA—3OE**, with a tri(oxyethylene) spacer, was also prepared but was found to have very poor solubility, and hence its solution properties could not be examined.
(36) All the spectral data are available in the Supporting Information.
(37) The fractionated samples exhibit unexpectedly high values of polydispersity and this is because of the presence of aggregates at the concentrations used for GPC (~2 mg/cm^3), as evidenced from the light scattering detector signal. Ultrasonication of the solutions prior to injection reduces the high molecular tail but does not completely remove it.
(38) In our earlier study,[30] we had shown that the spectral changes seen in the nascent polymer **PDA—6OE** were very similar to those seen in the high molecular weight fractionated samples. Similarly, representative studies using fractionated samples of the other two polymers were also done, which helped reaffirm the earlier observations.
(39) Polyimides from pyromellitic dianhydride and simple amine terminated oligo(oxyethylene)s were prepared as controls and these were white in color.
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(41) For an earlier report on the effect of spacer length on CT interactions in small molecule D−A systems see: Verhoeven, J. W.; Dirkx, I. P.; Boer, T. J. *Tetrahedron Lett.* **1966**, 4399.
(42) Comparison of the temperature dependences of the UV−visible and NMR spectra of the polymer **PDA—5OE** with the corresponding model DA−5OE in the presence of excess Li^+ ion (see Figure S13 in Supporting Information) provides further evidence in support of the hypothesis that while the NMR chemical shifts are sensitive to the presence of sandwiched structures and reflects the formation of extended stacked structures in the polymer, the CT absorbance fails to detect this stacking. Since in the DA model only simple pairing can occur but not extended stacking, one sees a smaller change in the δ values compared to that seen in the polymer, while the variations in the CT absorbance in both systems are almost parallel.
(43) The higher the stability of the fully folded state when compared to the unfolded one, the greater would be the temperature-dependence of the equilibrium constant; i.e., one would expect the equilibrium to shift more toward the fully folded form as one reduces the temperature.
(44) The solvent effect was examined using methanol/chloroform mixtures as it exhibited a larger effect on folding, while an aprotic solvent mixture, such as acetonitrile/chloroform mixture, is more suitable for metal-ion titration studies.
(45) The effect of counterion was examined in a ^{1}H NMR titration study of **PDA—5OE**, using $NaClO_4$ and NaSCN, and no significant difference was noticed.
(46) The spectral changes of **PDA—5OE** and **PDA—6OE** with increasing concentrations of various alkali-metal ions are provided in the Supporting Information. The variation of the spectral features in the aliphatic region in these spectra provides further direct evidence for the fact that the complexation indeed occurs with the OE spacer. The nonuniform changes in the aliphatic region (some of the peaks move upfield while others move downfield) of the spectra confirms that the variation in the chemical shift is not induced by changes in the dielectric (or ionic strength) of the medium but is a direct reflection of complexation. Formation of the CT complex between the donor and acceptor units could bring some of the methylene protons, particularly those close to the aromatic rings, under the influence of the aromatic ring current, and therefore further influencing their chemical shifts. Similar changes have been seen in the case of podands by Vogtle et al. See ref 26a.
(47) In **PDA—5OE**, the changes seen in the δ values of the acceptor protons in the presence of Li and Na are almost the same while changes in their UV−visible spectra are distinctly different. This is possibly because of differences in the geometries of the CT complexes formed upon complexation with Na and Li. The effect of differences in geometry appears to be more significant on the A_{CT}, but not on acceptor proton chemical shifts. This is confirmed from the model compound (**DAD—5OE**) studies, wherein the changes seen in the chemical shifts of the acceptor proton under similar conditions are roughly similar for both Na and Li (see Figure 10), although they exhibit distinct differences in their A_{CT}.
(48) We assume, of course, that the DAD and ADA model compounds readily form sandwiched structures in the presence of alkali-metal ions. This assumption is supported by the large difference in the NMR spectral variations between these models and the corresponding DA analogue.
(49) Similar changes in the proton NMR spectra of naphthalene donor containing adeamers were reported by Iverson and coworkers, and were ascribed to differences in the geometries of the D−A complexes. See ref 22c.
(50) When the donor is sandwiched both the aromatic rings of the naphthalene unit it experiences similar changes and remains undifferentiated.
(51) Dynamic light scattering studies on a representative polymer, **PDA—6OE**, revealed that a dramatic narrowing of the size distribution occurred in the presence of an excess of K ion, possibly reflecting the breaking of aggregated structures, which was also seen in the GPC chromatograms. However, a quantitative estimate of extent of stacking could not be obtained.

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