Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 3183–3192 **3183**
DOI: 10.1021/ma100189q

Folding a Polymer via Two-Point Interaction with an External Folding Agent: Use of H-Bonding and Charge-Transfer Interactions

Swati De, Debasis Koley, and S. Ramakrishnan*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

Received November 27, 2009; Revised Manuscript Received February 22, 2010

ABSTRACT: A polymer containing electron-rich aromatic donors (1,5-dialkoxynaphthalene (DAN)) was coerced into a folded state by an external folding agent that contained an electron-deficient aromatic acceptor (pyromellitic diimide (PDI)) unit. The donor-containing polymer was designed to carry a tertiary amine moiety in the linking segment, which served as an H-bonding site for reinforcing the interaction with the acceptor containing folding agent that also bore a carboxylic acid group. The H-bonding interaction of the carboxylic acid and the tertiary amine brings the PDI unit between two adjacent DAN units along the polymer backbone to induce charge-transfer (C-T) interactions, and this in turn causes the polymer chain to form a pleated structure. Evidence for the formation of such a pleated structure was obtained from NMR titration studies and also by monitoring the C-T band in their UV−visible spectra. By varying the length of the segment that links the PDI acceptor to the carboxylic acid group, we showed that the most effective folding agent was the one that had a single carbon spacer, as evident from the highest value of the association constant. Control experiments with propionic acid clearly demonstrated the importance of the additional C-T interactions for generating the folded structures. Further, solution viscosity measurements in the presence of varying amounts of the folding agent revealed a gradual stiffening of the chain in the case of the PDI carrying carboxylic acid, whereas no such affect was seen in the case of simple propionic acid. These observations were supported by DFT calculations of the interactions of a dimeric model of the polymer with the various folding agents; here too the stability of the complex was seen to be highest in the case of the single carbon spacer.

Introduction

Controlling the conformation of polymer chains in solution is a challenge that is not only exciting from a purely academic standpoint but it also holds the potential to spatially arrange functional units around a polymer backbone and consequently elicit unique collective properties that rely on such specific arrangement. Whereas folding of well-defined oligomers[1] has been extensively studied using a variety of directional intrachain interactions, such as H-bonding,[2] π-stacking,[3] metal-ion interactions,[4] charge-transfer complexation,[5] etc., efforts to extend this to higher molecular weight polymers have been far more limited. Some years ago, we designed a few such polymeric systems wherein charge-transfer interactions between alternatingly placed electron-rich dialkoxynaphthalene (DAN) and electron-deficient pyromellitic diimide (PDI) units, aided by metal-ion complexation and solvophobic interactions, caused the polymer chain to adopt a specific folded conformation.[6] Such charge-transfer (C-T) induced folding was first studied by Iverson and co-workers[5a−g] in well-defined oligomers and more recently elaborated by Zhao et al.[5h] to generate alternate designs to fold oligomeric systems. In all these studies, the C-T interactions served not only to assist folding but it also served as a valuable spectroscopic signature to study the folding process. Extending our approach further, we designed a polymer carrying only PDI acceptor units linked by oligo(oxyethylene) segments, which was then made to fold upon interaction with a small molecule bearing a DAN donor unit and an ammonium group.[7] In this approach, a two-point interaction: one between the ammonium group and the oligo(oxyethylene) segment and the other a C-T interaction between the DAN donors and PDI acceptor units, caused the polymer chain to adopt a pleated structure leading to the generation of D−A stacks. The association constant between the folding agent and the polymer was estimated to be around 850 M^{-1}, which implied that the extent of folding was limited to only about five to six D−A pairs. In an attempt to enhance the association constant and extend the stacking further, we designed a new type of donor containing polymer that carries a tertiary amine unit in the spacer segment, which could interact strongly with a suitably designed acceptor-bearing folding agent that also carries a carboxylic acid group, as shown in Scheme 1. This acid−base interaction, we reasoned, would bring the acceptor unit in a suitable position so as to form a C-T complex with the adjacent donors, resulting in the folding of the polymer chain. The structure of the folding agent, specifically the length of the segment that links the carboxylic acid to the DAN unit, was varied to optimize the folding efficacy.

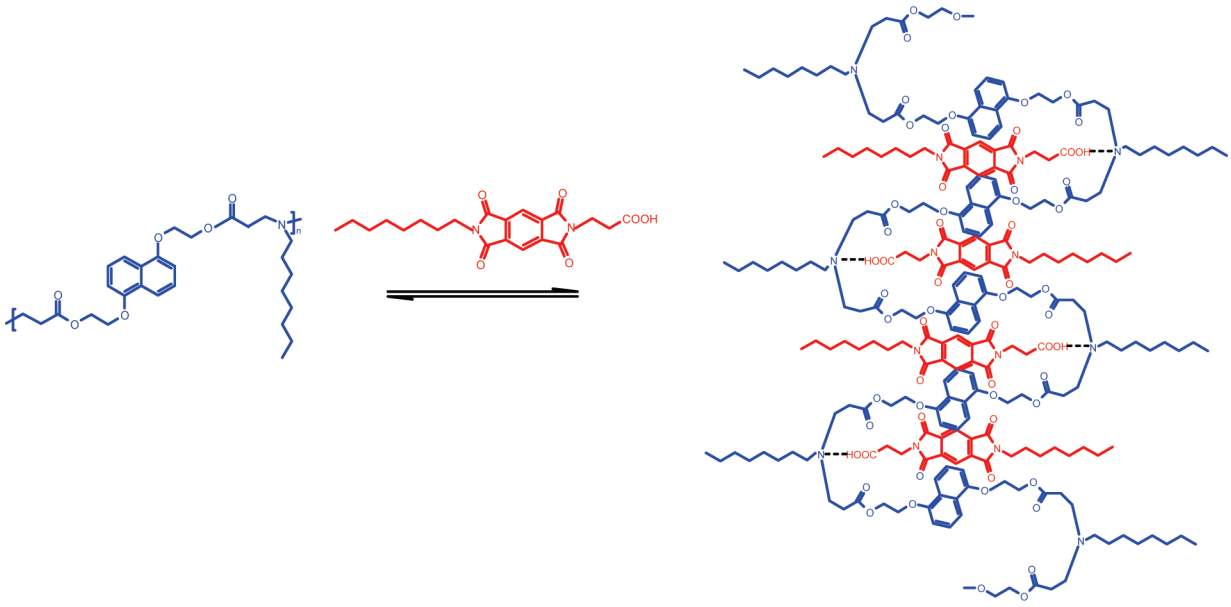
Experimental Section

1,5-Dihydroxynaphthalene, pyromellitic dianhydride and acryloyl chloride were purchased from Aldrich Chemical Co. Pyromellitic dianhydride was refluxed with dry-distilled acetic anhydride before use. All the solvents were dried following the standard procedures.[8] Structures of all intermediates, monomers and polymers were confirmed by ^{1}H NMR spectroscopy. NMR spectra were recorded on a Bruker AV400 MHz spectrometer, using $CDCl_3$ as the solvent and TMS as reference. GPC measurements were carried out using Viscotek triple detector system (TDA model 300), coupled to a refractive index (RI), a right-angle light scattering (RALS) and a differential viscometer (DV) in series. The separation was achieved using a series of two PL gel mixed bed columns (300 × 7.5 mm) operated at 30 °C using THF

*Corresponding author. E-mail: raman@ipc.iisc.ernet.in.

Published on Web 03/05/2010

Scheme 1. Schematic Representation of Folding Aided by Two-Point Interactions with a Folding Agent



as the eluent. Molecular weights were determined using the light scattering calibration curve based on the data from the RI, DV and RALS detectors. The UV−visible (UV−vis) spectra were recorded using a Varian 300 UV spectrophotometer.

Synthesis of Compound 4. 1,5-Dihydroxynaphthalene **1** (1.5 g, 9.38 mmol) was taken along with K_2CO_3 (6.4 g, 46.4 mmol) and a catalytic amount of KI in dry acetonitrile (25 mL) and stirred for 1 h. Then, chloroethanol acetate (4.6 g, 37.5 mmol) was added and the contents were refluxed for 72 h at 100 °C. After the reaction was complete, CH_3CN was removed, and the contents were poured in alkaline water. The residue formed was filtered and dried to get compound **3**, which was then directly used for the next step without further purification. Compound **3** was taken with K_2CO_3 (3.0 g) in a mixture of dry MeOH (15 mL) and dry THF (15 mL) and stirred for 12 h at 50 °C. Then, the solvents were removed, and the residue poured in basic water. The precipitate formed was filtered and dried to give 1.4 g (overall yield = 61%) of compound **4**. mp 130 °C. ^{1}H NMR (δ, $CDCl_3$): 2.0 (t, 2H, CH_2**OH**), 4.0 (m, 4H, −**CH_2**OH), 4.2 (t, 4H, Ar−O−**CH_2**CH_2OH), 6.8 (d, 2H, Ar−**H**, *o*-OCH_2), 7.3 (t, 2H, Ar−**H**, *m*-OCH_2), 7.8 (2H, Ar−**H**, *p*-OCH_2).

Synthesis of Compound 5.[9] Compound **4** (1.0 g, 4.0 mmol) was taken in dry THF (5 mL) and stirred in ice−water bath for 5 min. Then, Et_3N (2.0 g, 19.8 mmol) was added dropwise. After 30 min, acryloyl chloride (1.82 g, 20.0 mmol) in dry THF (5 mL) was added dropwise. The reaction mixture was stirred at room temperature for 3 h, followed by stirring at 50 °C for 7 h. After the reaction was complete, THF was removed, and the contents were poured in acidic ice-cold water. The residue was then filtered, dried, and purified by column chromatography to get 0.44 g of compound **5** (yield = 30%). mp 80 °C. ^{1}H NMR (δ, $CDCl_3$): 4.3 (t, 4H, Ar−O−**CH_2**CH_2OCO), 4.6 (t, 4H, −**CH_2**OCO), 5.8 and 6.4 (d, 2H each, =**CH_2**), 6.1 (m, 2H, −OCO**CH**=), 6.8 (d, 2H, Ar−**H**, *o*-OCH_2), 7.3 (t, 2H, Ar−**H**, *m*-OCH_2), 7.8 (2H, Ar−**H**, *p*-OCH_2).

Synthesis of Polymer (P). Diacrylate **5** (0.38 g, 1.06 mmol) was dissolved in 3 mL of a mixture of dry THF and dry DMF (5:1 v/v). Octyl amine (0.137 g, 1.06 mmol) was added, and the reaction mixture was stirred in a sealed vessel at 50 °C for 15 days. The reaction mixture was then poured in methanol, and the precipitate formed was dissolved in a minimum amount of THF and reprecipitated in MeOH once again to get 0.310 g (yield = 60%) of polymer **P**. M_w = 23 000 and M_n = 19 000 using light scattering calibration. ^{1}H NMR (δ, $CDCl_3$): 0.8 (t, 3H, −N(CH_2)$_7$**CH_3**), 1.27 (m, 12H, −NCH_2(**CH_2**)$_6$$CH_3$), 2.3 (t, 2H, −N**$CH_2$**($CH_2$)$_6$$CH_3$), 2.4 (t, 4H, −$OCOCH_2$**$CH_2$**), 2.8 (t, 4H, −OCO**$CH_2$**$CH_2$), 4.2 (t, 4H, Ar−O−**$CH_2$**$CH_2$OCO), 4.5 (t, 4H, −**$CH_2$**OCO), 6.7 (d, 2H, Ar−**H**, *o*-OCH_2), 7.3 (t, 2H, Ar−**H**, *m*-OCH_2), 7.8 (2H, Ar−**H**, *p*-OCH_2).

Synthesis of Model Compound (M). Monoacrylate **6**[10] (0.30 g, 1.10 mmol) was dissolved in 2.5 mL of a mixture of dry THF and dry DMF (4:1 v/v). *n*-Octyl amine (0.071 g, 0.55 mmol) was added, and the reaction mixture was stirred in a sealed vessel at 50 °C for 15 days. The solvent was then removed, and the contents were poured in water. It was then extracted with EtOAc, and the organic layer was washed with brine. EtOAc was removed, and the product was recrystallized from a mixture of methanol and chloroform (2: 1 v/v) to get 0.27 g (yield = 73%) of model compound **M**. ^{1}H NMR (δ, $CDCl_3$): 0.8 (t, 3H, −N(CH_2)$_7$**CH_3**), 1.27 (m, 12H, −NCH_2(**CH_2**)$_6$$CH_3$), 2.3 (t, 2H, −N**$CH_2$**($CH_2$)$_6$$CH_3$), 2.4 (t, 4H, −$OCOCH_2$**$CH_2$**), 2.7 (t, 4H, −OCO**$CH_2$**$CH_2$), 3.93 (s, 3H, −O**$CH_3$**), 4.2 (t, 4H, Ar−O−**$CH_2$**$CH_2$OCO), 4.47 (t, 4H −**$CH_2$**OCO), 6.76 (m, 2H, Ar-**H**, *o*-OCH_3 and *o*-OCH_2), 7.3 (m, 2H, Ar−**H**, *m*-OCH_3 and m-OCH_2), 7.8 (m, 2H, Ar−**H**, *p*-OCH_3 and *p*-OCH_2).

Synthesis of Compound PDI-C1.[5i,j] Pyromellitic dianhydride (1.0 g, 4.5 mmol) was taken in dry DMF (15 mL) along with glycine (0.338 g, 4.5 mmol) and octyl amine (0.592 g, 4.5 mmol). The contents were stirred for 12 h at 100 °C, after which the DMF was removed under reduced pressure and the residue was purified by column chromatography to get 0.540 g of compound **PDI-C1** (yield = 32%). mp 240−245 °C. ^{1}H NMR (δ, $CDCl_3$): 0.90 (t, 3H, −NCH_2CH_2-(CH_2)$_5$**CH_3**), 1.35 (m, 10H, −NCH_2CH_2 (**CH_2**)$_5$$CH_3$), 1.71 (m, 2H, −$NCH_2$**$CH_2$**($CH_2$)$_5$$CH_3$), 3.77 (t, 2H, −N**$CH_2$**$CH_2$($CH_2$)$_5$$CH_3$), 4.57 (s, 2H, −N**$CH_2$**COOH), 8.3 (s, 2H, Ar−**H**).

Synthesis of Compound PDI-C2. PDI-C2 was synthesized following the same procedure as that of **PDI-C1** using β-alanine instead of glycine. Yield = 31%, m.p. = 230−232 °C. ^{1}H NMR (δ, $CDCl_3$): 0.83 (t, 3H, −NCH_2CH_2(CH_2)$_5$**CH_3**), 1.27 (m, 10H, −NCH_2CH_2 (**CH_2**)$_5$$CH_3$), 1.6 (m, 2H, −$NCH_2$**$CH_2$**($CH_2$)$_5$$CH_3$), 2.8 (t, 2H, NCH_2**CH_2**COOH),3.7 (t, 2H, −N**CH_2**CH_2(CH_2)$_5$-CH_3), 4.03 (t, 2H, N**CH_2**CH_2COOH), 8.22 (s, 2H, Ar−**H**).

Synthesis of Compound PDI-C3. PDI-C3 was synthesized following the same procedure as that of **PDI-C1** using 4-aminobutyric acid instead of glycine. Yield = 30%, mp 216 °C. ^{1}H NMR (δ, $CDCl_3$): 0.87 (t, 3H, −NCH_2CH_2(CH_2)$_5$-**CH_3**), 1.27 (m, 10H, −NCH_2CH_2 (**CH_2**)$_5$$CH_3$), 1.69 (m, 2H, −$NCH_2$**$CH_2$**($CH_2$)$_5$$CH_3$), 2.07 (m, 2H, −$NCH_2$**$CH_2$**$CH_2$-COOH), 2.46 (t, 2H, −$NCH_2CH_2$**$CH_2$**COOH), 3.75 (t, 2H, −N**CH_2**CH_2(CH_2)$_5$$CH_3$), 3.85 (t, 2H, −N**$CH_2$**$CH_2CH_2$COOH), 8.27 (s, 2H, Ar−**H**).

Folding Studies. For a typical NMR titration experiment, 2 mL of the polymer solution (2 mM) was prepared in a mixture of $CDCl_3$ and MeOH (20:1 v/v; solution **A**). An aliquot of this solution (0.6 mL) was taken in the NMR tube, and a large excess (~10−15 equiv) of the acceptor folding agent was dissolved in the remaining solution to form solution **B**. Solution **A** was then titrated with solution **B** (in 20−100 μL steps), which resulted in a series of solutions having fixed polymer concentration but with varying amounts of the acceptor. The UV−vis titration experiments were similarly performed using a mixture of $CHCl_3$ and MeOH (20:1) as the solvent. The spectra in Figure 5 were obtained by subtraction of the pure polymer spectrum from that of the spectrum of the mixture (polymer + folding agent) to permit clear visualization of the C-T band.

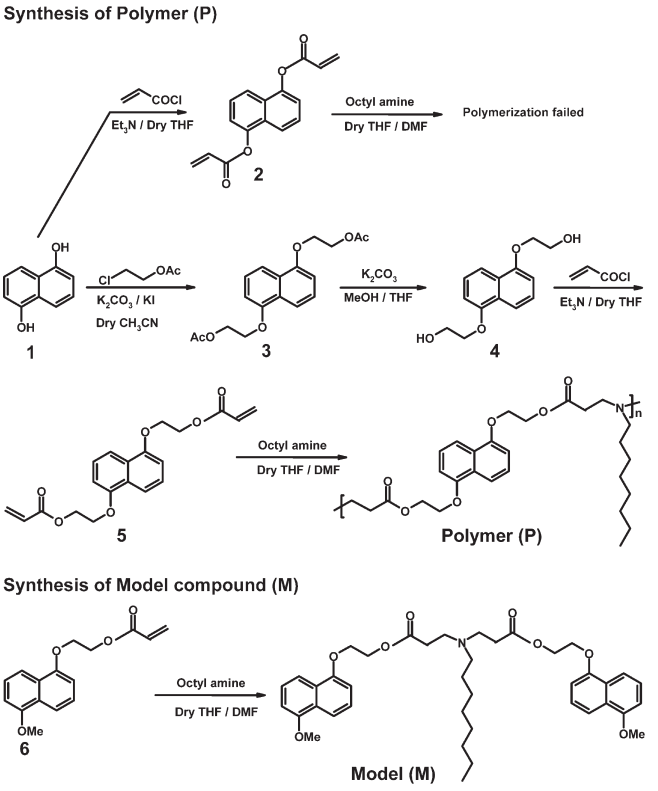
Viscosity Measurements. For viscosity measurements, 20 mL of the polymer solution (10 mg/mL) was prepared in a mixture of $CHCl_3$ and MeOH (20:1 v/v; solution **A**). An aliquot of this solution (4 mL) was taken with an excess (5 equiv) of the folding agent **PDI-C1** (or propionic acid) to make up solution **B**. Both solutions were filtered using a 0.5 μm membrane filter prior to the measurement. Viscosity measurements were carried out by mixing different volumes of two solutions, which resulted in a series of solutions having fixed polymer concentration but with varying amounts of the folding agent (or carboxylic acid). The measurements were done using an Ubelhode viscometer immersed in a constant temperature bath maintained at 25 °C. The flow times were measured using an automated Schott Gerate instrument.

Computational Details. All DFT calculations were performed using Gaussian03 program package.[11] The density functional calculations with the Becke's half-and-half functional (BH&H)[12] employed a basis set of double-ζ quality, which is denoted LANL2DZ in Gaussian. The elements C, N, O, and H were described by a Dunning/Huzinaga full double-ζ basis set.[13] The BH&H functional was employed because of its ability to characterize adequately dispersion interactions.[14] Geometries were fully optimized, normally without symmetry constraints. Harmonic force constants were computed at the optimized geometries to characterize the stationary points as minima. Zero-point vibrational corrections were determined from the harmonic vibrational frequencies to convert the total energies, E_e, to ground-state energies, E_0. The rigid-rotor harmonic oscillator approximation was applied to evaluate the thermal and entropic contributions. Single-point solvent calculations were performed on the optimized gas-phase geometries of our model compounds and the corresponding complexes. We employed the CPCM model,[15] which is an implementation of the conductor-like screening model (COSMO)[16] in Gaussian03. $CHCl_3$ (ε = 4.9) was used as a solvent with UAKS (united atom topological model) radii scheme for the respective atoms (C, H, N, and O). Enthalpy ($\Delta H_{298(sol)}$) and free energy ($\Delta G_{298(sol)}$) change in $CHCl_3$ were calculated from the solvent electronic energy (ΔE_{sol}) and respective thermal corrections from gas-phase thermochemical values. (Refer to the Supporting Information.) The effect of basis set superposition error (BSSE) on the BH&H/LANL2DZ binding energies was determined through the counterpoise method of Boys and Bernardi.[17] The TDDFT (time-dependent density functional theory)[11] singlet excitation energies of the complexes in chloroform were evaluated by a recent nonequilibrium implementation of the CPCM model.[16] To characterize the C-T bands, only the five lowest spin-allowed singlet−singlet transitions were taken into account. Transition energies and oscillator strengths were interpolated by a Gaussian convolution with a width of 0.2 eV.[18]

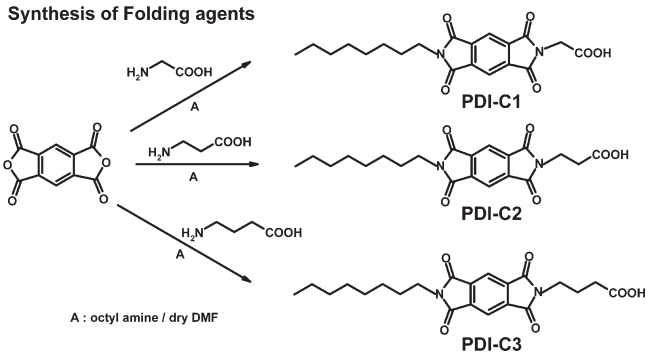
Results and Discussion

Michael addition has been extensively used for the preparation of dendrimers and, more recently, for the preparation of linear and hyperbranched polymers.[19] Although these polymerizations

Scheme 2. Synthetic Scheme for the Preparation of the Donor Containing Polymer (P) and Model Compound (M)



Scheme 3. Synthetic Scheme for the Preparation of the Acceptor Containing Folding Agents (PDI-C1, PDI-C2, and PDI-C3)



are relatively slow, polymers of moderate-to-high molecular weights have been attained using this approach. Because Michael-addition based polymerizations generate polymers bearing tertiary amine groups along the polymer backbone, we chose to use this appraoch for the present study. Therefore, to prepare a linear polymer containing electron-rich aromatic donors linked by a segment that carries a tertiary amine group, we synthesized a donor containing diacrylate monomer (to serve as a Michael acceptor) and reacted it with an aliphatic primary amine. The two active hydrogens in the primary amine would be expected to add to the acrylate units to yield the polymer (**P**) (Scheme 2). Although the reactivity of a primary and secondary amine (formed after the first addition) toward Michael addition is different, it is of little consequence in the present context because of the symmetry of the final polymer structure. In our first attempt, we used a simple diacrylate (**2**) of 1,5-dihydroxynaphthalene and reacted it with *n*-octylamine in order to generate the polymer. However, the aryl acrylate linkage was very susceptible to cleavage; therefore, the polymerization process did not

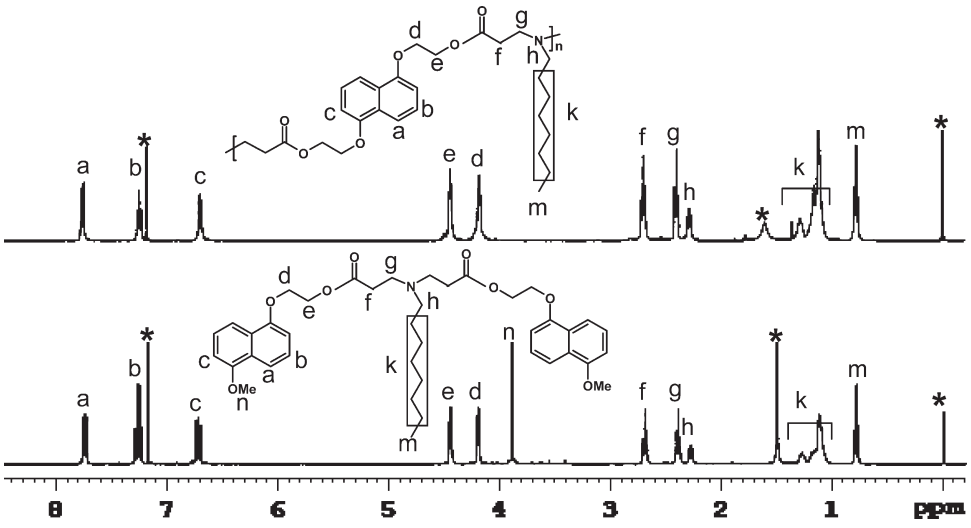


Figure 1. ^{1}H NMR spectra of the polymer (**P**) and model compound (**M**) in $CDCl_3$. The peaks marked by asterisk are due to solvent or inadvertent water.

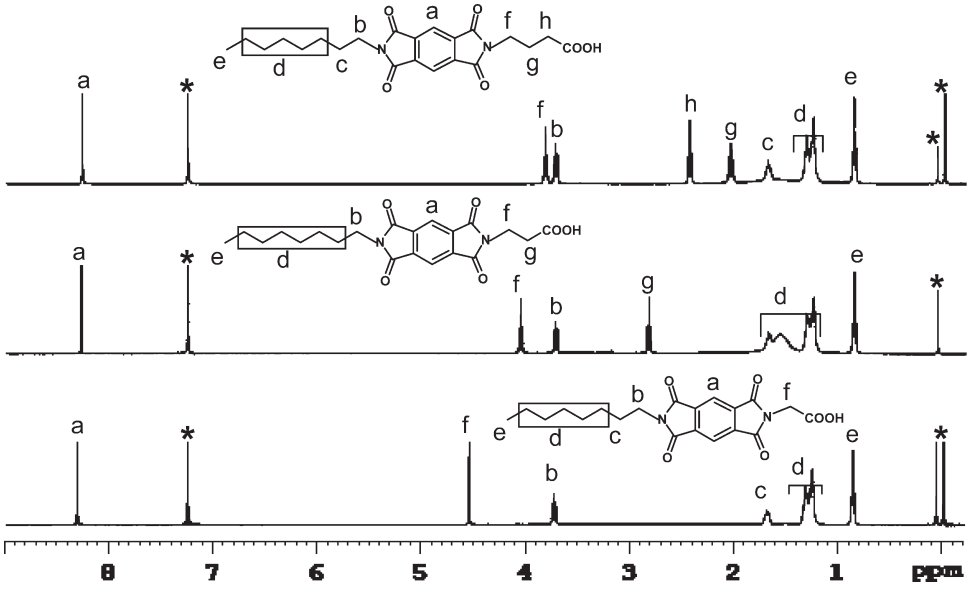


Figure 2. ^{1}H NMR spectra of the acceptor containing folding agents (**PDI-C1**, **PDI-C2**, and **PDI-C3**) in $CDCl_3$. The peaks marked by asterisk are due to solvent or inadvertent water.

occur effectively. Hence, we incorporated an ethylene spacer segment by coupling the 1,5-dihydroxynaphthalene to chloroethanol acetate, followed by hydrolysis and coupling to acryloyl chloride. (See Scheme 2.) The reaction of the spacer containing monomer (**5**) with *n*-octylamine yielded the polymer (**P**), having a moderately high molecular weight of M_w = 23 000 and M_n = 19 000 using the triple detector system. The *n*-octyl group on the amine serves to enhance the polymer solubility; furthermore, the relatively high boiling point of the amine ensured that the stoichiometric balance between the two monomers was not significantly altered during the prolonged polymerization at 50 °C. It is expected that the length of the spacer segment would influence the stability of the folded state; the additional four methylene units in this design, we argued, may provide greater flexibility and facilitate adaptation to the preferred geometry of the C-T complex formed with the external acceptor, although the configurational entropy cost for folding is expected to increase. Three acid-containing folding agents, bearing varying lengths of the spacer linking the PDI and the acid group, were synthesized (as per the Scheme 3) by reacting pyromellitic dianhydride with an equimolar mixture of the appropriate amino acid and *n*-octylamine. The required product was readily separated from the mixture of the three possible products and typically was obtained in ~30% yield. For a comparative study of the folding process, a model compound (**M**) that represents the smallest foldable unit of the polymer was also prepared as per the Scheme 2.[10]

The proton NMR spectra of the polymer (**P**) and the model compound (**M**) are shown in Figure 1, along with the peak assignments. The long chain octyl pendant group ensured adequate solubility of the polymer in common organic solvents, which is essential to carry out the folding studies. The relative intensities of the various peaks were in accordance with the expected structure. Three sets of peaks corresponding to the aromatic protons of the naphthalene ring are seen in the spectrum of the polymer, and these have been assigned as indicated in the Figure; the most downfield peak (peak a) corresponds to the proton para to the alkoxy substituent.[20] The model compound also exhibited a very similar spectrum, except for the additional peak due to the terminal methoxyl protons at 3.9 ppm. The NMR spectra of the PDI carrying acceptors, **PDI-C1**, **PDI-C2**,

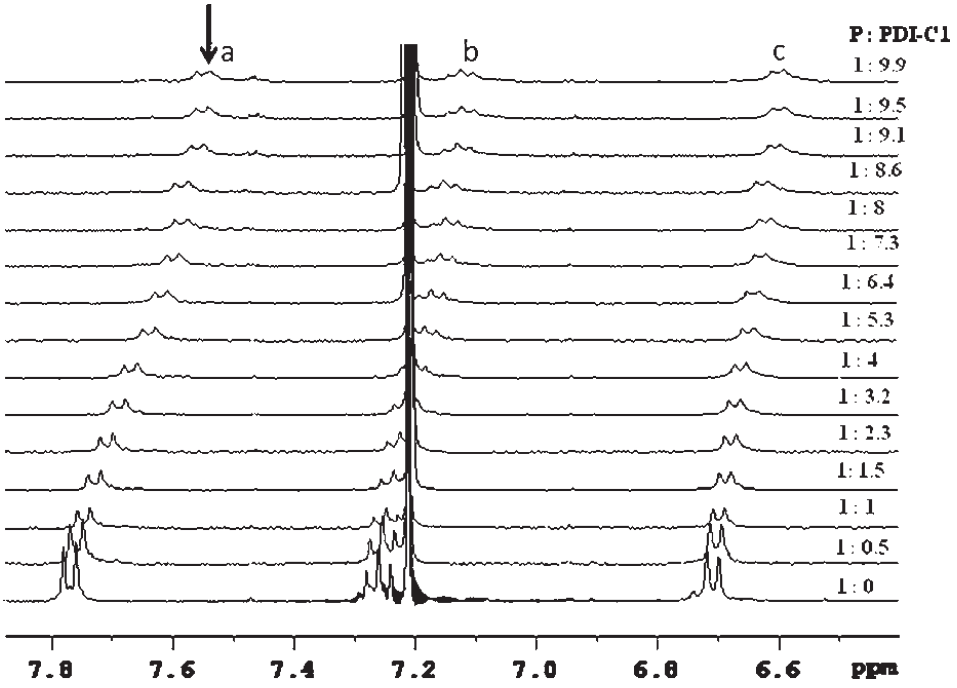


Figure 3. Variation in the aromatic region of the ^{1}H NMR spectra of polymer **P** as a function of increasing amounts of an acceptor containing folding agent, **PDI-C1**. The δ value of peak a, marked by an arrow was monitored to study the folding. A 2 mM solution of **P** in $CDCl_3$/MeOH mixture (20:1, v/v) was used for the titration.

and **PDI-C3**, are shown in Figure 2 along with their peak assignments.

To study the folding of the polymer in the presence of the folding agent, we carried out NMR titration experiments wherein the relative mole ratio of the polymer and folding agent was varied. As previously shown,[6,7] the chemical shift of the donor and acceptor protons is very sensitive to the formation of a C-T complex; the chemical shift of the aromatic protons of both the donor and acceptor units shifts upfield, the effect on the acceptor proton typically being a little more pronounced. In Figure 3, we show the variation in the aromatic region of the proton NMR spectra of mixtures of the polymer **P** and folding agent **PDI-C1** as a function of increasing mole ratio of folding agent. It is evident that all three sets of aromatic peaks belonging to the polymer DAN unit experience an upfield shift with increasing concentration of folding agent, although the maximum shift is experienced by the most downfield proton (peak a), which we shall henceforth use to monitor the extent of folding. The titration of the model compound **M** also shows a similar behavior, as evident from Figure S3 of the Supporting Information; here again the maximum shift is seen for the most downfield proton. As shown by Sanders et al.,[20] this difference in the relative sensitivity of the different protons of the DAN unit is a reflection of the precise geometry of the C-T complex. The folding experiments were done in a mixture of $CDCl_3$ and methanol (20:1, v/v), keeping the methanol content to the minimum required to ensure that both the components are completely soluble. The strength of the interaction between the folding agent and the polymer has been previously shown to be greater in solvent mixtures of lower polarity because of the solvophobic effect on the polymer conformation that facilitates complex formation.[21]

To optimize the process of folding, three folding agents bearing spacers of different length between the acceptor and the carboxylic acid group were prepared. Similar NMR titration experiments were also carried out using the other two folding agents, and the variation of the chemical shift of the most downfield aromatic proton (peak a) of the donor as a function of mole ratio of the folding agents was plotted (Figure 4a). As is evident, the

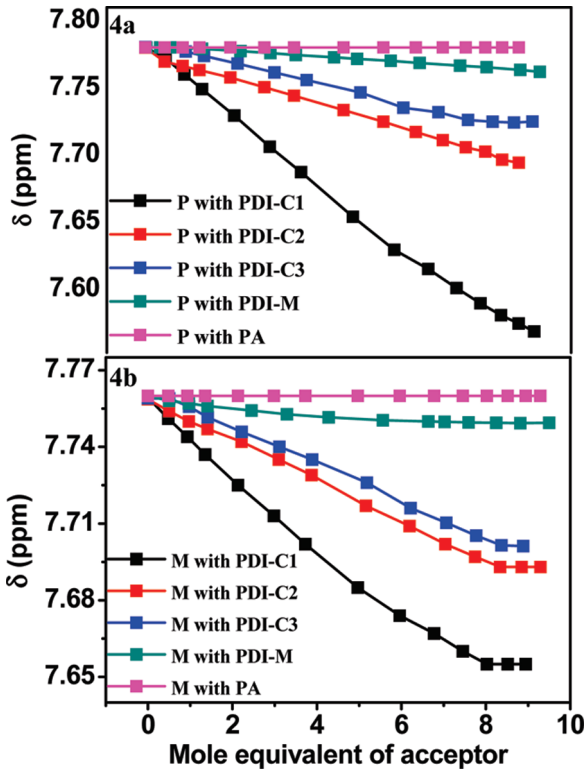


Figure 4. Variation in the chemical shift (δ) of peak a of (a) the polymer **P** and (b) the model compound **M** in the presence of various folding agents **PDI-C1**, **PDI-C2**, **PDI-C3**, **PDI-M**, and **PA**. Solutions (2 mM) of the **P** and **M** in $CDCl_3$/MeOH mixture (20:1, v/v) were used for all the studies.

maximum change in the chemical shift is observed when **PDI-C1**, bearing a single carbon linker between the **PDI** and the carboxylic acid, was used as the folding agent. When longer spacers, **C2** and **C3**, are present, the change observed in the chemical shifts is

Table 1. Association Constants (K_a) for Complexes Were Calculated by Using EQNMR Version 2.10 and from UV-Dilution Experiment

no.	molecule	K_a from EQNMR (M^{-1})	K_a from UV dilution experiment (M^{-1})	extinction coefficient (M^{-1} cm^{-1})
1	**P** with **PDI-C1**	1200	1325	40.5
2	**P** with **PDI-C2**	800	593	37.8
3	**P** with **PDI-C3**	300	[a]	[a]
4	**M** with **PDI-C1**	815	1170	33.5
5	**M** with **PDI-C2**	520	592	30.3
6	**M** with **PDI-C3**	128	[a]	[a]

[a] C-T band was too weak to carry out the dilution experiements.

significantly smaller. A nonlinear least-squares fitting procedure using EQNMR[22] permitted the determination of the association constants under the rapid exchange limit, and these values are listed in Table 1. It is clear from the numbers that **PDI-C1** is most effective in inducing the polymer to fold; the association constant was found to be ~1200 M^{-1}, whereas the other two folding agents exhibited significantly lower values. A similar plot in the case of the model compounds (Figure 4b) also revealed that **PDI-C1** exhibited the highest association constant, followed by **PDI-C2** and **PDI-C3**. A further interesting observation is that the association constant was smaller in the model system when compared with the polymer in all three cases, suggesting that the solvophobic effect may be significantly higher in the polymeric systems than in the model compound. In other words, the addition of methanol (a nonsolvent for the polymer) modulates the polymer conformation toward one that spatially co-locates adjacent donor units and consequently enhances C-T complex formation with the folding agent, whereas such an effect is expectedly much smaller in the case of the model compound. To ascertain the importance of the C-T interaction in the folding process, a control titration was carried out wherein the polymer was titrated with increasing amounts of simple carboxylic acid, namely, propionic acid (**PA**). The chemical shift of the most downfield donor protons was unaffected by the presence of propionic acid, suggesting that little, if any, interaction between the adjacent DAN units occurs. A similar titration using bis(*n*-propyl)-pyromellitic dimide (**PDI-M**) also showed very little variation of the δ value, which confirmed the importance of the additional H-bonding interaction. (See Figure 4.) These experiments taken together reveal the importance of the two-point interaction in enabling the formation of the pleated structure.[23] Comparative examination of their solution viscosities, as will be discussed later, further confirms the importance of both the interactions in stiffening the polymer chain.

The C-T complex formation can also be readily studied by monitoring the C-T band in the absorption spectra. Figure 5a depicts the variation of the absorption spectra, in the region where the C-T transition occurs, with increasing mole fraction of the folding agent. A similar plot using the model compound with the folding agent is shown in Figure 5b. The variation of the A_{CT} at λ_{max} was plotted as a function of folding agent mole ratio for the different folding agents, and these are shown as insets in Figure 5. It is clear that the most instense C-T band is seen in the case of **PDI-C1**, followed by **PDI-C2** and **PDI-C3**, which is generally in agreement with the trend seen in the NMR titrations.

UV dilution experiments[24] were done to determine the association constants between the polymer and different folding agents; the values thus obtained are listed in Table 1. The UV dilution experiments also provided an estimate of the molar extinction coefficient associated with the C-T band, and these are also listed in Table 1. The association constant values obtained from NMR and UV dilution studies are in reasonable agreement, thus reaffirming the conclusions that the efficacy of folding agents follows the trend **PDI-C1** > **PDI-C2** > **PDI-C3**. In the case of

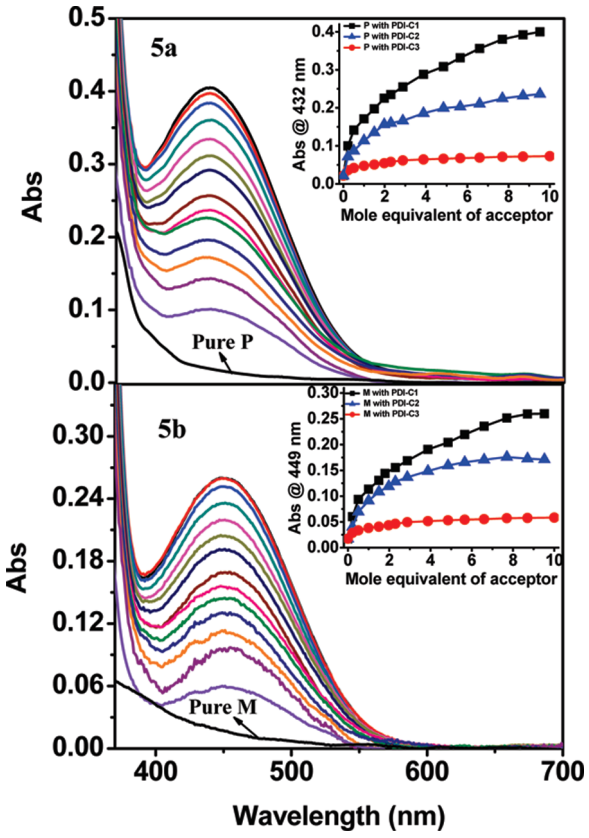


Figure 5. Variation of the UV−vis spectra of (a) polymer **P** and (b) model compound **M** as a function of increasing amounts of the folding agent, **PDI-C1**. Insets: variation of the absorbance of the C-T band of the polymer **P** (inset a) and model compound **M** (inset b) as a function of increasing amounts of the folding agents: **PDI-C1**, **PDI-C2**, and **PDI-C3**. Solutions of **P** and **M** (2 mM) in $CHCl_3$/MeOH mixture (20:1, v/v) were used for all studies.

PDI-C3, the UV dilution studies were difficult to perform because of very low intensity of charge transfer band, and hence the association constant value could not be determined.

Whereas the spectral changes seen in the NMR and UV−vis studies suggest the formation of a pleated structure, it would be useful to measure other chain conformational properties to confirm this. To do so, we carried out solution viscosity measurements of the polymer solution (1 wt %) in the presence of increasing amounts of the folding agent, **PDI-C1**; the variation of the inherent viscosity is plotted as a function of mole ratio of the folding agent in Figure 6. It is clearly evident that a dramatic increase in the solution viscosity is seen to occur beyond a threshold concentration of the folding agent. This observation suggests a stiffening of the chain on going from a flexible random coil to a pleated structure. A control titration experiment was also done wherein a similar experiment was performed in the presence of a simple carboxylic acid, namely, propionic acid (**PA**). The H-bonding of this carboxylic acid with the amine units along the backbone alone is clearly inadequate to cause the conformational transition, as evident from the very small increase in the inherent viscosity (Figure 6); the additional C-T interactions between the DAN units along the polymer backbone and the PDI unit of the folding agent is essential to further stabilize the folded form.

In an effort to rationalize the observed trend in the folding efficacy of the three folding agents, we carried out computational studies using DFT methods. These studies were carried out for the interaction of the model compound **M**′ with each of the folding agents (**C1**′, **C2**′, **C3**′); for ease of computation, the *N*-alkyl group in both cases was taken as a methyl instead of

the *n*-octyl, which is present in the actual systems. The BH&H/LANL2DZ-optimized structures of the three donor−acceptor complexes are shown in Figure 7. From the top view of the optimized structures, it is evident that the most symmetric placement of the donors on either side of the central acceptor unit is seen in the case of **M′-C1′**, whereas in both of the other cases, the two donors are staggered and shifted off-center with respect to the central acceptor unit. The BSSE-corrected energetics for the formation of the complexes in chloroform ($CHCl_3$) are given in Table 2. In each of the complexes (**M′-C1′**, **M′-C2′**, and **M′-C3′**), both hydrogen bonding (N3· · · ·H1−O5) as well as C-T interactions are dominant. The free energy ($\Delta G_{298(sol)}$) of formation for the complexes are in the order **M′-C1′** > **M′-C2′** > **M′-C3′** (Table 2), which is in accordance with the trend observed in the experimental values of formation constants. (See Table 1.)

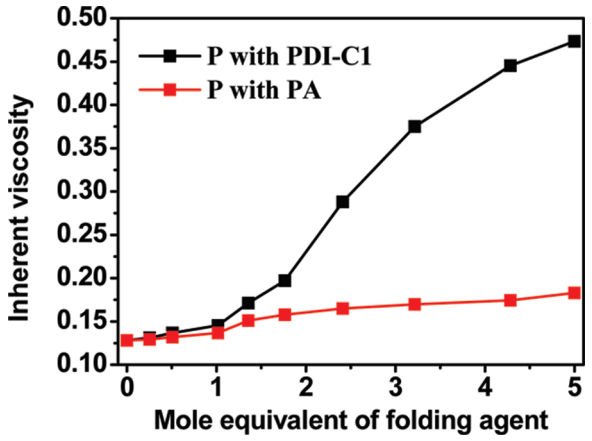


Figure 6. Variation of the inherent viscosity of polymer **P** as a function of increasing amounts of the folding agent, **PDI-C1**, or propionic acid (**PA**). The polymer concentration was maintained at 1 wt % in $CHCl_3$/MeOH mixture (20:1, v/v), whereas the mole ratio of **PDI-C1** or **PA** (with respect to the polymer repeat unit) was varied.

To separate the contributions of the N3· · ·H1−O5 hydrogen bonding interaction from those of $\pi-\pi$ stacking (C-T), a series of single-point BH&H/LANL2DZ calculations were performed. Scheme 4 displays the approach utilized to separate out the contribution from the two different interactions toward the overall stabilization of the complexes. To retrieve the relative contributions, the donor−acceptor complexes can be analyzed under two different decomposition schemes (step A and step B; see Scheme 4) that will furnish "incomplete complexes" **I** and **IV**. In step A (Scheme 4), the two donor fragments are removed without altering the relative orientations of the remaining constituents. Now, the fragmented complex **I** is composed of two independent subfragments **II** and **III**, which interact primarily through H-bonding. Therefore, the interaction energies obtained by subtracting the BSSE-corrected, single-point energies of **I** from those of **II** and **III** for each of the complexes **M′-C1′**,

Table 2. BH&H/LANL2DZ Calculated Binding Energies (kilocalories per mole) for the Complexes M′-C1′, M′-C2′, and M′-C3′[a,b]

complexes	ΔE_e	ΔE_0	ΔH_{298}	ΔG_{298}	ΔE_{sol}[c]	$\Delta H_{298(sol)}$	$\Delta G_{298(sol)}$
M′-C1′	−57.2	−55.8	−57.4	−30.1	−46.1	−46.3	−19.0
M′-C2′	−51.7	−50.5	−51.8	−25.7	−42.9	−43.0	−16.9
M′-C3′	−45.6	−44.7	−45.9	−20.2	−37.6	−37.9	−12.2

[a] ΔE_e is the electronic energy without the ZPE correction. ΔE_0 includes the ZPE correction. ΔE_{sol} is the solvent electronic energy. $\Delta H_{298(sol)}$ is the enthalpy change in $CHCl_3$ including the thermal enthalpic corrections from the gas phase. Similarly, $\Delta G_{298(sol)}$ is the free energy change in $CHCl_3$ including the thermal free energy corrections fom the gas phase. [b] All energies are counterpoise corrected. [c] In $CHCl_3$.

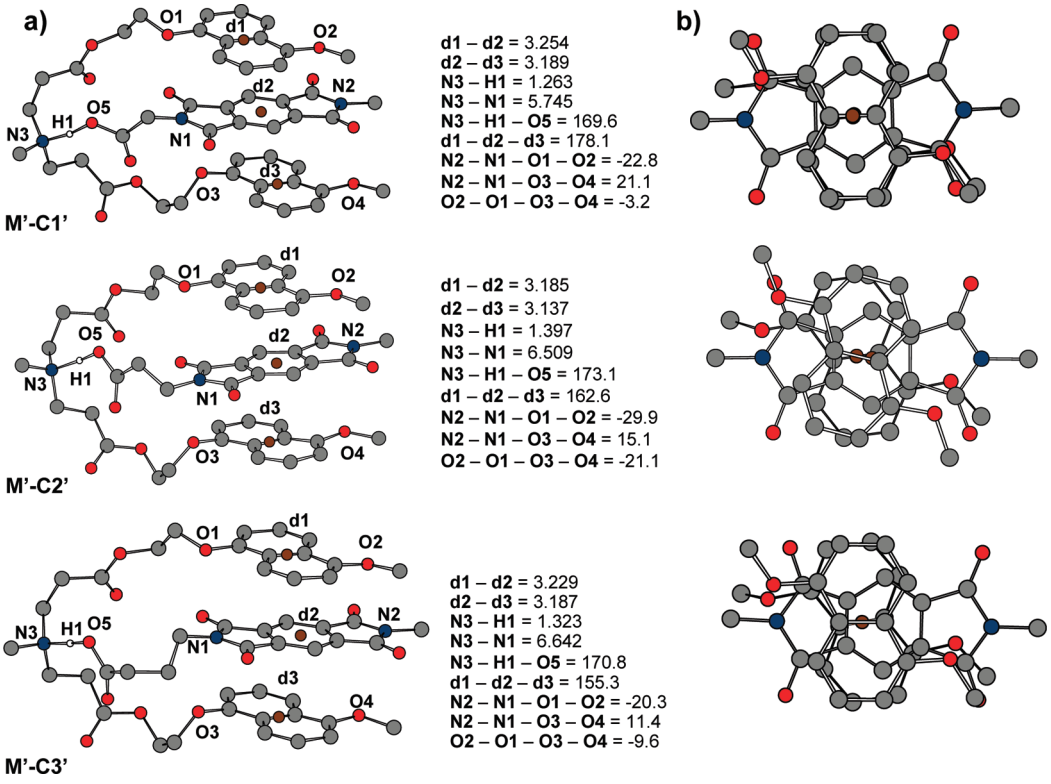


Figure 7. (a) Optimized structures of the model complexes **M′-C1′**, **M′-C2′**, and **M′-C3′** with selected bond lengths (in angstroms) and angles (in degrees). Hydrogen atoms of aromatic and spacer groups have been omitted for clarity. (b) Top view of the π-stacked aromatic framework for the three different complexes. Color code: C, gray; O, red; N, blue; center-of-mass (c.o.m.) of the aromatic segments, brown.

Scheme 4. Energy Fragmentation Schemes for the Donor−Acceptor Complexes

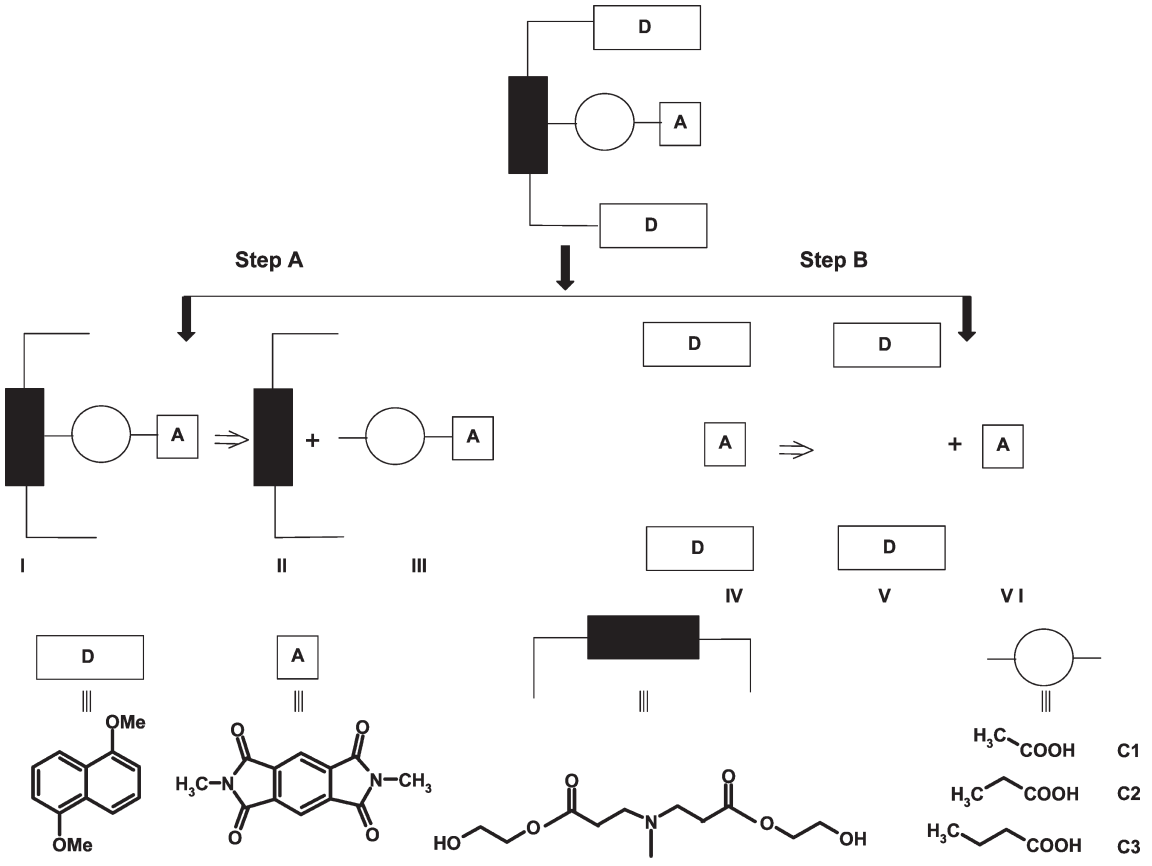


Table 3. Energies (kilocalories per mole)for the Fragmentation of the Complexes (M′-C1′, M′-C2′, and M′-C3′; See the Text) As Shown in Scheme 4[a]

complexes	H-bonding (step A)		π-stacking (step B)	
	ΔE_e	ΔE_{sol}[b]	ΔE_e	ΔE_{sol}[b]
M′-C1′	−58.5	−50.1	**M′-C1′**	−58.5
M′-C2′	−43.3	−35.6	**M′-C2′**	−43.3
M′-C3′	−48.7	−40.9	**M′-C3′**	−48.7

[a] All energies are counterpoise-corrected. [b] In $CHCl_3$.

M′-C2′, and **M′-C3′** (Table 3) yield the energies mainly associated with the formation of N···H−O hydrogen bonds.

Similarly, in step B, the spacer groups of the donor and acceptor units were removed, and only the aromatic fragments were retained, as in **IV**. To quantify the π-stacking (C-T) interaction, complex **IV** was separated into the two donors (**V**) and an acceptor (**VI**) (Scheme 4) moieties. The energies associated with this process correspond to the donor−acceptor C-T interaction energies, and the trend seen for the three complexes reveals that the strength varies in order **M′-C1′** > **M′-C2′** > **M′-C3′** (Table 3). From this simple decomposition process, it is evident that the final stability of the complex appears to be more dependent on the hydrogen bonding interaction between the acid moiety of the folding agent and the amine unit of the model rather than on the C-T interaction between the D and A units. A similar observation was reported by Houk et al. in their exhaustive study of the binding of bipyridinium-based guests by [3], [4] catenated hosts.[25] Interestingly, the H-bonding interaction in **M′-C3′** is stronger than **M′-C2′** (N3−H1 = 1.397 Å, ΔE_{sol} = −35.6 kcal/mol for **M′-C2′** versus N3−H1 = 1.323 Å, ΔE_{sol} = −40.9 kcal/mol for **M′-C3′**), although the overall stability of **M′-C3′** is lower than **M′-C2′**. (See Tables 2 and 3.) This is clearly reflected in the N3−H1 distances in the three complexes (1.263 (**M′-C1′**), 1.397 (**M′-C2′**), and 1.323 Å (**M′-C3′**), respectively). This apparent anomaly may be ascribed to the destabilization associated with the spacer segments, which accounts for the higher overall stability of **M′-C2′** when compared with **M′-C3′**. One other point in the present design is that the two-point interaction does not directly impose a conformational constraint on the flexible linking segment, unlike in our previous study where the interaction of the oligo(oxyethylene) spacer with an ammonium unit brings the adjacent PDI units in close proximity to the DAN unit in the folding agent, thereby enabling C-T-induced stacking.[7] Therefore, to assess the driving force for stacking in our system, we examined the energetics associated with the interaction of a preformed D−A pair with an additional donor unit to form a DAD stack. Calculations suggested an additional stabilization to the tune of about −13.9 kcal/mol,[26] thereby supporting the fact that the formation of the D-A stacks, as depicted in Scheme 1, indeed enhances the stability of the system.[27]

Time-dependent DFT calculations effectively capture the C-T interactions in the complexes. The oscillator strength (f) for the C-T excitation is highest for **M′-C1′** and lowest for the **M′-C3′** complex (**M′-C1′** (f = 0.0343), **M′-C2′** (f = 0.0327), **M′-C3′** (f = 0.0186)). Clearly, the intensity of the C-T excitation is influenced by the relative orientation of the donor and acceptor fragments.[28,5e,g] The geometry of the D−A−D complex can be analyzed by comparing a few of the key parameters of the energy minimized structures. First, the relative positions of the centers of mass (d1, d2, and d3) can be examined: the angle d1−d2−d3, which is a measure of their colinearity, was found to be 178.1, 162.6, and 155.3° for **M′-C1′**, **M′-C2′**, and **M′-C3′**, respectively (Figure 7a). Second, the relative orientations of the two DAN units can be gauged from the angle between the lines O1−O2 and O3−O4 (projected onto a single plane), which was determined

to be 3.2, 21.1, and 9.6° for for **M′-C1′**, **M′-C2′**, and **M′-C3′**, respectively. These values clearly indicate that the complex **M′-C1′** is the most symmetric one, whereas the other two complexes are significantly more asymmetric, although the origins of the asymmetry in each case is different. The significantly lower oscillator strength for the C-T transition in **M′-C3′**, when compared with the other two, could be a reflection of the lower symmetry of the complex, although the relatively close values of *f* in the other two cases suggest that other parameters could also be important in governing the oscillator strength of the C-T band. These values of *f* are qualitatively consistent with the variation of the extinction coefficients of the C-T band seen in these three cases (Table 1); the extinction coefficients in the cases of **PDI-C1** and **PDI-C2** are roughly similar, whereas in the case of **PDI-C3**, the C-T absorbance was too low to permit the dilution experiments; this possibly reflects the significantly lower value of the extinction coefficient, in addition to the lower K_a value in the case of **PDI-C3**.

In conclusion, we have developed a simple methodology for the preparation of a polymer carrying periodically placed electron-rich aromatic donors (DAN), wherein the spacer segment linking the units carries a tertiary amine unit. The polymer was made to fold by the interaction of a small-molecule folding agent that carries an electron-deficient aromatic acceptor (PDI) and a carboxylic acid. The formation of a pleated structure is facilitated by two interactions: H-bonding (N···H) between the amine nitrogen on the spacer and the carboxylic acid proton, which then enables the C-T interaction between the PDI unit and the two adjacent DAN units of the polymer chain. The length of spacer that links the carboxylic acid group to the PDI unit in the folding agent is shown to play a crucial role in governing the stability of this complex. Both NMR titration and UV−vis studies of the C-T band reveal that the folding agent that carries a C1 spacer forms significantly stronger complexes than the other two folding agents that carry C2 and C3 spacers, making it the most effective folding agent. Solution viscosity measurements of the polymer solution as a function of increasing mole ratio of the folding agent clearly revealed a sharp rise in the viscosity suggesting stiffening of the chain upon interaction with **PDI-C1**; such an increase was not seen when a simple carboxylic acid, such as propionic acid, was used, thereby confirming the importance of the additional C-T interaction for the formation of the pleated structure. DFT studies of the interaction of a model compound, which contains two DAN units linked by the same spacer segment (as in the polymer), and the different folding agents also show that the folding agent with a C1 spacer forms the most stable complex, wherein both the H-bonding and C-T interactions provide maximum stabilization. Although this design has enabled us to enhance the association constant (1200 M^{-1}) between the folding agent and the polymer when compared with our previous design,[7] wherein the interaction of an ammonium group of the folding agent with an hexa(oxyethylene) spacer (OE6) of the polymer assisted the formation of a pleated structure stabilized by C-T interactions, the increase was not very substantial. The computational assessment of the relative importance of the two interactions in the folding process provided us some broader insight into designing more effective approaches for generating folded structures. *Therefore, it might be useful to think of such two-point interaction-induced folding as being driven by a strong anchoring interaction* (*primary*) *between the polymer and the folding agent, which is then complemented by a secondary structure-generating, weaker but directional, interaction; in this case, H-bonding serves as the primary interaction, whereas the C-T interaction serves as the secondary one*. It is evident from these studies that alternate designs, wherein the primary interaction of the folding agent with the polymer is substantially stronger, needs to be developed to generate more stable folded conformations. Importantly, such efforts should enable one to translate the conformational control achieved in solution to the solid state. Work along these lines are presently being pursued.

Acknowledgment. We would like to thank the Department of Atomic Energy for the ORI-Award for the period 2006-2011. D.K. is indebted to the Indian Institute of Science for providing the Centenary Postdoctoral Fellowship and is grateful to the Supercomputer Education and Research Centre (SERC) for extending computational facilities.

Supporting Information Available: Experimental details of model monomer synthesis, NMR titrations, EQNMR fitting, UV−vis titrations, UV−vis dilution experiments, and computational details, such as absolute energies and optimized Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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