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Charge-Transfer Reinforced Folding of Novel Ionenes

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Ionenes[1] may be construed as polymers that are built-up by linking surfactant molecules in a head-to-tail fashion to generate long chains. The majority of the ionenes studied so far are cationic and carry quaternary ammonium groups. They are generally prepared by the reaction of a di-*tert*-amine with a dihalide under standard Menschutkin reaction[2] conditions to generate a polymer bearing periodic quaternary ammonium groups, either equally spaced (symmetric) or unequally spaced (unsymmetric) depending on the choice of the two monomers. Since the early studies by Rembaum and coworkers,[3] ionenes have fascinated researchers because they represent a class of polyelectrolytes wherein the charges reside directly on the polymer backbone and, importantly, the periodicity of the charges can be very easily controlled. A variety of ionenes, both symmetrical and unsymmetrical, have been investigated, and a fairly comprehensive understanding of their properties with regard to the length, stiffness, and hydrophobicity of the alkylene spacer segment, which lies between the ammonium groups, has been gained.[4] Early studies by Kunitake et al.[5] suggested that in symmetric ionenes bearing long alkylene spacers (>12 carbons), the polymer chain could adopt an accordion-type conformation (Scheme 1) in aqueous solutions. This idea was later exploited by Hinze et al.[6] using long chain ionenes to develop micelle-mimetic systems that were utilized for improved separation and chemical analysis. The incorporation of a rigid azobenzene unit within the alkylene segment was also shown to induce a similar transition to a folded accordion-type structure in a solvent of suitable polarity.[7] Incorporation of pendant semifluoroalkyl groups into ionenes led to the formation of layered domains in thin solid films.[8] Fluorescent probes, covalently linked as pendant units, have been used to study the conformational changes in ionenes as a function of various parameters, such as spacer segment, salt concentration, and so on.[9] One other interesting feature of ionenes is that their solution properties can also be modulated by the simple exchange of the counterion, which typically is a halide that can be exchanged for a variety of organic anions. The exchange of the halide counterion of ionenes with surfactants, such as lauryl sulfate, renders interesting micellar properties to these systems, the precise nature of which strongly depends on the extent of counterion exchange.[10] In recent times, cationically charged polyelectrolytes, including ionenes, have been investigated for their potential to serve as gene-delivery vehicles because of their ability to form complexes with oppositely charged DNA.[11] In essence, it is clear that ionenes form an interesting class of easily synthesizable polymers whose solution conformation and solid-state properties can be modulated by simple structural manipulations involving either the periodicity of the charges or the nature of the counterions.

Control of polymer conformation in solution has attracted a great deal of attention in recent times because of the motivation of researchers to emulate the exquisite conformational control exercised in biomacromolecular systems to achieve a desired function. Foldamers[12] form an interesting class of macromolecules that change their conformation in a predetermined manner in response to external stimuli, such as solvent polarity, temperature, ionic strength, added metal ion, and so on. Whereas the major focus of these studies has been well-defined oligomers, relatively fewer reports have explored flexible high-molecular-weight polymers that possess greater conformational freedom.[13] Some years ago, we designed polymeric systems wherein charge-transfer (CT) interactions between alternatingly placed electron-rich donor (D) and electron-deficient acceptor (A) units, aided by metal-ion complexation and solvophobic interactions, caused the polymer chain to adopt a specific folded conformation.[14] Such charge-transfer-induced folding was first studied by Iverson and coworkers[15] in well-defined oligomers and was later elaborated by Zhao et al.[16] to generate alternate designs to fold oligomeric systems. In all of these studies, the CT interactions served not only to assist the folding process but also as a valuable spectroscopic signature to study the folding process. In the present study, we have combined design elements from ionenes with those of charge-transfer complexation to develop novel foldamers, wherein the propensity to form accordion-type structures is reinforced by charge-transfer interactions that further stabilize the folded form, as depicted in Scheme 1. A particularly interesting feature of this system is the high sensitivity of their solution color to solvent polarity.

Synthesis and Structural Characterization. Ionenes are typically synthesized by the reaction of an α,ω-dibromoalkane with an α,ω-bis(*N*,*N*-dimethylamino)alkane.[3] This approach can be readily modified to yield several interesting ionenes that bear various types of functional units within the alkylene segment of either or both the of monomers. Several examples of ionenes that carry functional units, such as azobenzene,[7] bipyridine,[17] anthracene,[18] porphyrin,[19] and so on, have been reported. In the present study, we utilized a di-*tert* amine monomer (**A**) carrying a dialkoxynaphthalene (DAN) donor unit and a dibromide monomer (**B**) bearing a pyromellitic diimide (PDI) acceptor unit. Monomer **A** was prepared by first alkylating 1,5-dihydroxynaphthalene using an excess of 1,6-dibromohexane to yield 1,5-bis(6-bromohexyloxy)naphthalene, which was then treated with excess dimethylamine to yield the desired monomer. Monomer **B** was synthesized by reacting pyromellitic anhydride with a little over 2 equiv of 6-aminohexanol, followed by transformation of the terminal hydroxyl groups using PBr_3.[20] Polymerization was carried out by taking equivalent amounts of the two monomers in a chloroform−methanol solvent mixture (2:1 v/v) in a sealed tube and heating it to 90 °C for 36 h. The concentration of the monomers was kept high to minimize the formation of cyclic products. The polymer was isolated by precipitation into diethyl ether and further purified by two reprecipitations using chloroform/methanol (1:1 v/v) as the solvent and diethyl ether as the nonsolvent.

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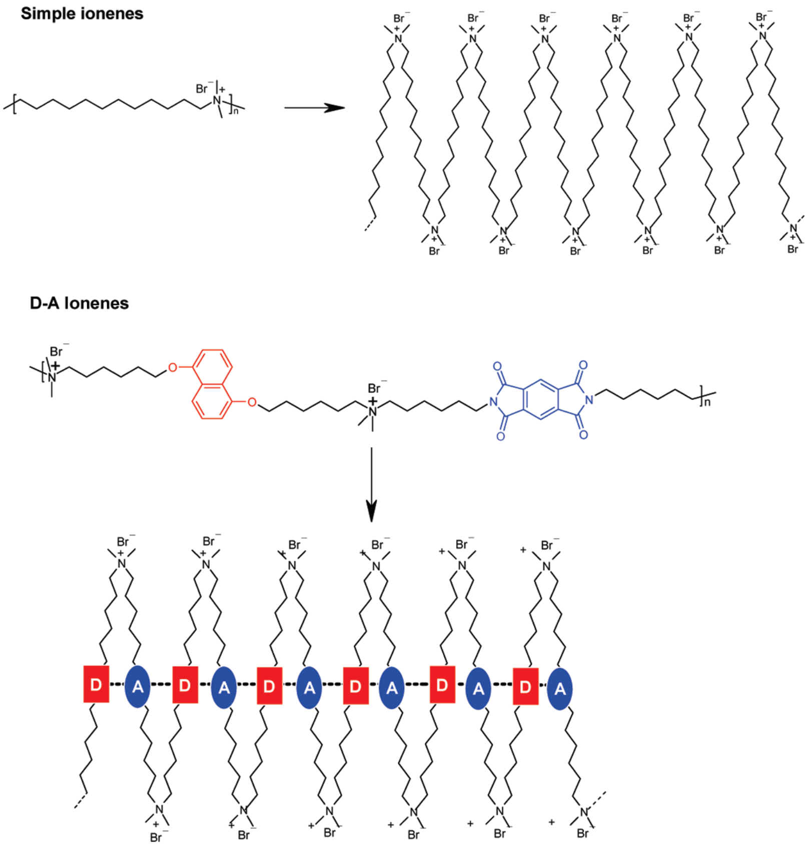
Scheme 1. Schematic Depiction of Folding of Ionenes and D−A Ionenes



The product was obtained as a brick-red powder after the purification. Its structure was confirmed by its proton NMR spectrum.[20] The molecular weight of the polymer was determined to be around 45 000 (M_w) by dynamic light scattering measurements in water.

Solvent-Induced Conformational Transition. The polymer was soluble in several solvents, such as water, methanol, DMSO, acetonitrile, and other polar organic solvents. Interestingly, the color appeared very different in different solvents: in water it was deep-red, whereas in acetonitrile, it was light-yellow, suggesting that the extent of charge-transfer was significantly different in solvents of different polarity. The UV−visible spectra of the D−A ionene solutions at a fixed concentration in four different solvents are shown in Figure 1. The intensity of the charge-transfer band increases dramatically with an increase in solvent polarity. The inset is a picture of the polymer solutions (2 mM) in water and in acetonitrile, which shows this dramatic difference.

Ionenes bearing long alkylene units (> 12 carbons), such as 16,16-ionene, is postulated to undergo a transition from an expanded coil to a folded accordion-type conformation (Scheme 1) upon increasing the solvent polarity.[5,6] This conformational transition occurs because of the interplay between two factors, namely, the electrostatic repulsion between the ammonium cations that keeps the chain expanded in less-polar solvents and the hydrophobic effects that cause the chain to fold in polar solvents to preclude exposure of the long alkylene segments to the polar medium. In our D−A ionenes, such a conformational transition is further reinforced by the formation of charge-transfer complex between the dialkoxynaphthalene donor (D) and the pyromellitic diimide acceptor (A) units, which in turn also provides a useful spectroscopic signal to monitor the transition. Despite the fact that the intrinsic D−A charge transfer interaction may be less favored in polar solvents,[21] the dominant factor that leads to an increase in the CT band is the influence of solvent polarity on the polymer chain conformation, which in this case brings the donor and acceptor units in closer proximity in polar solvents. The extent of folding clearly depends on the polarity of the solvent, and consequently, the intensity of the charge-transfer band is very high in water, whereas it is weak in acetonitrile.[22] Dilution experiments were done to confirm that the charge-transfer interaction is an intrachain and not an interchain process. The variation in absorbance as a function of concentration in three of the solvents is plotted in Figure 1b. Two conclusions can be drawn from these plots: one is that the charge-transfer interaction is indeed an intrachain process possibly leading to the postulated folded form, and the second is that the apparent extinction coefficients, as reflected by the slopes, strongly depend on the solvent polarity. The linear variation also reaffirms that dilution has a minimal effect on the chain conformation; therefore, the extent of D−A interactions within a single chain remains nearly constant with dilution. In principle, the solvent dependence of the apparent molar extinction coefficient of the CT band is both a reflection of the difference in the population of D−A pairs (because of the dependence of chain conformation on solvent polarity) and due to the intrinsic effect of solvent polarity on the oscillator strength of the transition. Earlier studies[23] have suggested that the extinction coefficient of the CT band is not very sensitive to solvent polarity, and our preliminary calculations also reaffirm this observation.[20] Therefore, we believe that the dominant factor for the observed enhancement in the CT band is the extent to which the solvent modulates the polymer chain conformation leading it toward a pleated structure, which in turn enhances the probability of charge-transfer

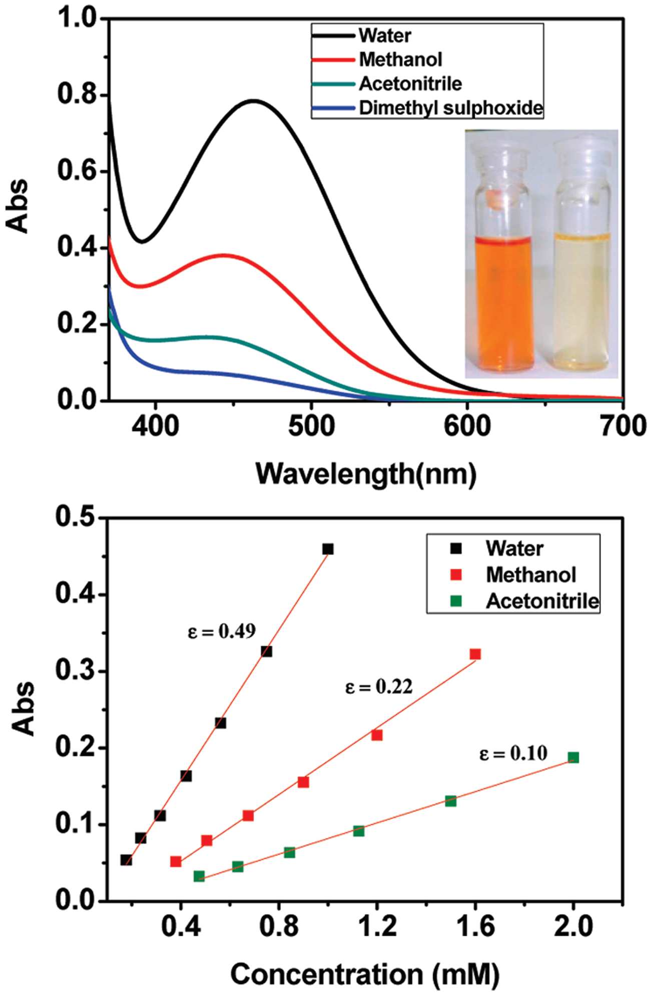


Figure 1. (a) UV−visible spectrum of a 2 mM D−A ionene polymer solution in different solvents (top). (b) Variation of absorbance (at λ_{max}) as a function of concentration in different solvents (bottom). Inset: A photograph of the D−A ionene solutions in water (left) and acetonitrile (right).

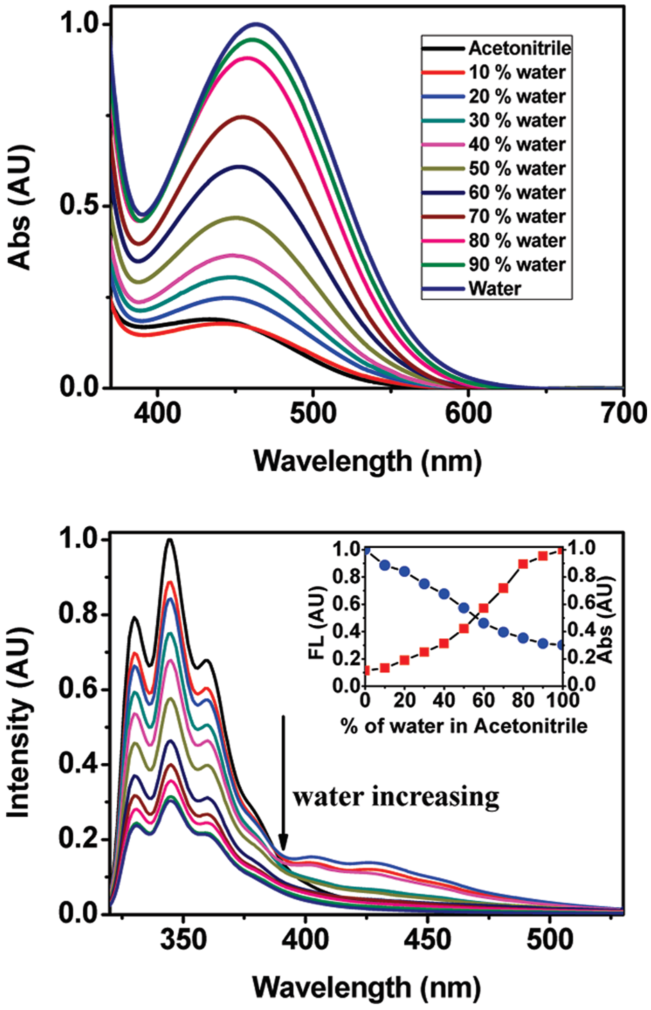


Figure 2. (a) UV−visible solvent-titration studies done by mixing different volumes of 2 mM polymer solutions in water and acetonitrile. (b) Fluorescence solvent-titration studies done similarly using 0.01 mM polymer solutions in water and acetonitrile. Inset depicts the variation in normalized absorbance and fluorescence intensity (at λ_{max}) as a function of solvent composition.

complex formation. The ratio of the slopes, therefore, is more of a reflection of the relative extent of folding in different solvents, suggesting that the extent of folding is roughly five times greater in water as compared with acetonitrile (ε_{water} = 0.49 mM^{-1} and ε_{acn} = 0.10 mM^{-1}).

A gradual collapse of the polymer chain can also be affected by solvent titration. The D−A ionene was taken in acetonitrile and titrated with water. As evident from Figure 2a, as the volume fraction of water increases, the intensity of the charge-transfer band also increases; this again is a reflection of a gradual folding of the polymer chain leading to increasing numbers of intrachain D−A charge-transfer complex formation. The donor, 1,5-dialkoxynaphthalene, is also fluorescent, and it is known that the fluorescence is significantly quenched upon the formation of a CT complex because of enhanced nonradiative decay pathways via the low-lying CT excited states.[15c] Fluorescence being a much more sensitive method, we examined the changes in fluorescence spectra under very dilute conditions (0.01 mM) as a function of solvent composition. As expected, a clear decrease in the emission intensity is seen with increase in solvent polarity (Figure 2b). The observed changes in the absorption and fluorescence spectra were normalized, and the variations as a function of solvent composition are shown in the inset in Figure 2b.The intensity of the CT band increases by nearly 10-fold, whereas the fluorescence from the dialkoxynaphthalene unit is seen to decrease substantially. Although the effect on the fluorescence intensity is slightly less drastic, the ability to sense the polarity at a much lower concentration should serve as an added advantage.

Effect of Temperature and Ionic Strength. The variation of the absorption spectra of an aqueous solution of the D−A ionene as a function of temperature are shown in Figure 3, which clearly shows a significant decrease in the CT absorbance with an increase in temperature. A plot of the variation of the CT absorbance as a function of temperature is shown in the inset. The decrease in the absorbance clearly suggests that the folded chain undergoes an expansion causing a weakening of the charge-transfer interaction and consequently to a lowering of the intensity of the charge-transfer band. A van't Hoff plot of this variation permitted the estimation of the ε value for the CT band in water, which was found to be ~800 M^{-1}.[24] This is roughly similar to the values reported in the case of rotaxanes that carry the same donor and acceptor units.[25] An increase in the ionic strength of the medium, by the addition of sodium chloride, similarly leads to a small but significant increase in the CT band intensity (see the Supporting Information). In this case, a further squeezing of the collapsed chain occurs because of

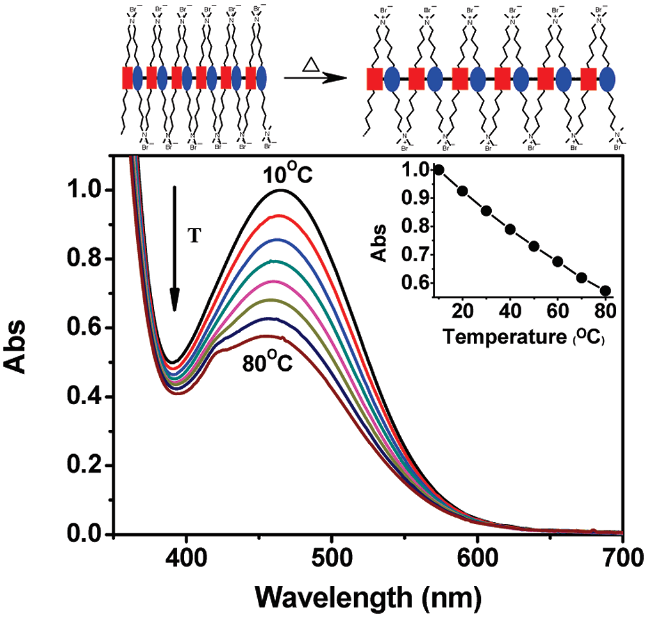


Figure 3. Variable temperature UV–visible studies done using a 2 mM aqueous polymer solution. Inset: Absorbance at 466 nm versus temperature. A schematic representation of the conformational change with temperature is also depicted.

the effective screening of the electrostatic repulsion between the ammonium head groups.

Visualizing the Collapsed Chains. In an effort to view the collapsed aggregates directly, we carried out atomic force microscopic measurements by drop casting a dilute aqueous solution of the D–A ionene onto a mica plate, followed by complete drying. A typical atomic force microscopic (AFM) image (Figure 4) clearly depicts the formation of circular aggregates. Careful line scans of these aggregates clearly reveal their disc-like nature; the height of the aggregates were typically around 3 to 4 nm, although their diameters varied greatly from 50 to 160 nm. The relative population of larger aggregates increases with increasing concentration of the casting solution. The thickness of the folded accordion-type structure (as depicted in Figure 4), estimated using the average length of the energy-minimized structures of the two repeat units taking the bromide ion diameter to be 3.8 Å, was found to be ~36 Å, which is remarkably close to the observed thickness in the AFM pictures.[26] This further strengthens the hypothesis that the collapse of the D–A ionenes is indeed occurring in the manner depicted in Scheme 1 to form cylindrical bundles whose top and bottom surfaces bear the charges. These bundles could then further aggregate laterally to form flat pancake-like structures that are seen in the AFM image.

In conclusion, we have described the design and synthesis of a novel class of ionenes that carry alternating electron-rich and electron-deficient aromatic units within the alkylene segments. The donor and acceptor units were incorporated at the centers of the alkylene segments, which enabled them to form charge-transfer complexes when the polymer chain was made to fold in a zigzag manner in a polar medium. Absorbance and fluorescence measurements provided unequivocal evidence of the formation of the charge-transfer complex, the extent of which is significantly enhanced in polar solvents. In water, the solvophobically driven collapsed state of the ionene chain is further stabilized by these charge-transfer interactions between the donor and acceptor units. AFM studies of films cast from dilute aqueous solutions of the D–A ionene clearly show the presence of flat pancake-like aggregates having uniform average thickness of ~3.5 nm, whereas their diameters were significantly larger, ranging from 50 to 160 nm. The close match of their thickness with the calculated value of 3.6 nm provided credence to the postulated accordion-type folding, whereas their large diameters suggest the occurrence of further lateral aggregation of individually collapsed chains. In light of the growing interest in single-chain polymeric nanoparticles,[27] the fully collapsed D–A ionenes could be viewed as polymeric nanoparticles that are stitched together by reversible weak noncovalent interactions. A recent study from Meijer's group[28] similarly examined the use of another reversible interaction, namely, multiple H-bonding, to induce reversible single-chain nanoparticle formation. One major difference of our system is the more structured collapse unlike the random collapse that is postulated in Meijer's example, although the CT interactions are admittedly far weaker compared with the quadruple H-bonding. Importantly, the collapsed ionene-based structures provide cationically charged molecular surfaces that could potentially add value both in terms of their use in electrostatic layer-by-layer assembly[7,29] as well as for use as sites to anchor other oppositely charged functional organic counterions. Explorations along these lines are currently underway.

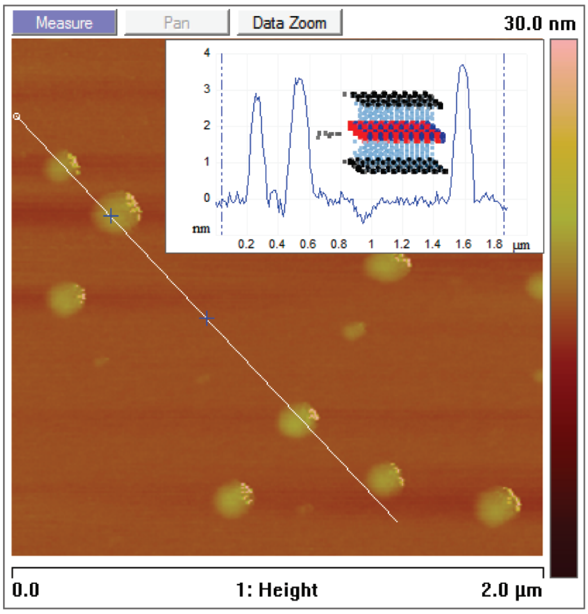


Figure 4. AFM micrograph showing pancake-like aggregates of D–A ionenes. The inset shows a line scan depicting the heights and diameters of the aggregates along with a schematic depiction of the aggregate.

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Supporting Information Available: Experimental details of monomer synthesis, polymerization procedure, spectral characterization, computational methods, and energy minimized structures of repeat units. This material is available free of charge via the Internet at http://pubs.acs.org.

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