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SYNTHESIS AND ION-BINDING PROPERTIES OF POLYMERIC PSEUDOCROWN ETHERS II: TEMPLATE ION INDUCED CYCLIZATION OF OLIGOMERIC ETHYLENE GLYCOL DIACRYLATES

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ABSTRACT

Inexpensive polymeric pseudocrown ethers have been synthesized based upon a "template ion" effect in which oligomeric ethylene glycol diacrylates are induced to assume a circular conformation in which the unsaturated end-groups are in proximity. This synthetic scheme has considerable potential for the development of inexpensive materials for binding of target cations. In this contribution we report a spectroscopic study of the induced cyclization caused by ion-dipole interactions between the templating cation and the electron lone pairs of the ethylene glycol ether linkages. Fluorescence spectroscopy was used to provide insight into the templatization process by examining excimer formation in pyrene end-labeled oligomeric ethylene glycol both in the absence and in the presence of the templating ion. Pyrene end-labeled tetraethylene glycol and pentaethylene glycol were synthesized and excimer fluorescence enhancement was studied with the introduction of cations such as nickel, chromium and tin in solvents such as tetrahydrofuran and chloroform. An increase in excimer fluorescence indicated enhanced excimer formation due to the templating effect of the cation which results in the end groups being close to each other. Molecular dynamics simulations of pyrene end-labeled ligands were performed to elucidate the effect of the large fluorescent chromophores on the chain conformations.

INTRODUCTION

Previously we proposed a novel synthetic scheme (1) for the synthesis of polymeric pseudocrown ethers which have potential applications in cation binding,

separations, and waste management. This scheme is based upon the tendency of oligomeric ethylene glycol diacrylates to assume circular conformations in the presence of templating cations. This templatization phenomenon may induce the diacrylate unsaturated end-groups to be in proximity. If a free-radical polymerization is initiated with a comonomer such as hydroxy ethyl methacrylate, both double bonds of such a templating oligomer may be incorporated into the same kinetic chain resulting in the formation of pendent loops. The probability of cyclization is increased if the polymerization is carried out in non-polar solvents in which the cation itself is insoluble thus ensuring maximum templatization and hence primary loop formation. Furthermore, if the free-radical polymerization is performed in dilute solution, the probability of cyclization is enhanced and would result in reduced crosslinking and more cyclization as shown in Figure 1.

Our previous solubility and ^{1}H NMR studies demonstrated that various cations were solubilized by oligomeric ethylene glycols (1) by virtue of ion-dipole interactions between the cation and the electron lone pairs of the ether linkages. Further, molecular dynamics simulations were performed on oligomeric ethylene glycol diacrylates both in the presence and absence of templating cations. A reduction in the mean end-to-end distance in the presence of a cation was observed (1) due to ion-induced constraints on the possible number and type of conformations adopted by the oligomer. These simulations affirmed the role of the templating ion in the synthetic scheme. In our present work we seek experimental corroboration of the theoretical results suggesting that templatization brings the chain ends into proximity.

Pyrene has been extensively used as a molecular probe due to its excellent fluorescence properties and its ability to form bi-molecular complexes (excimers) which fluoresce in a different spectral region than the individual "monomer" pyrene molecules. Cuniberti and Perico (2) were the among the first to study polymer cyclization using steady-state pyrene excimer fluorescence. These investigators synthesized pyrene end-labeled poly(ethylene oxide) and studied the influence of molecular weight on the extent of intramolecular excimer formation. They observed an increase in the intramolecular excimer fluorescence intensity with decreasing molecular weight. Winnik *et al.* (3,4) studied the cyclization dynamics of pyrene end-labeled polystyrene and demonstrated that intramolecular excimer formation could be observed only for chains containing less than 1000 to 2000 bonds. For higher molecular weight chains the rate constant for

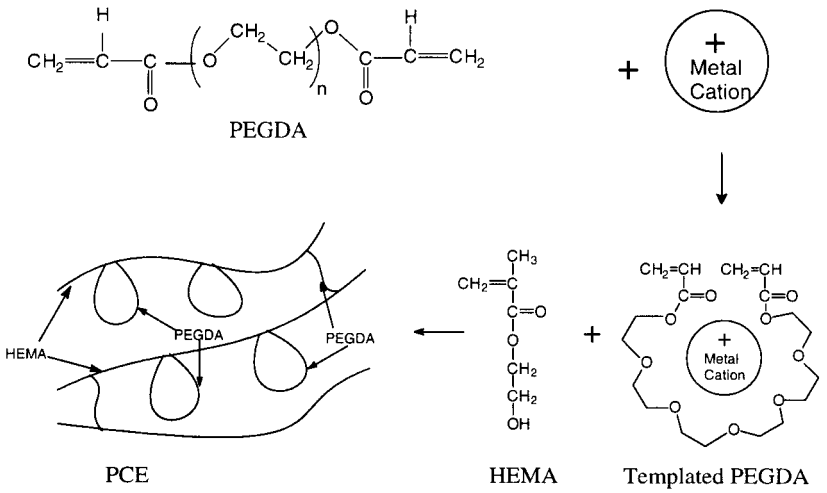

FIGURE 1. Novel synthesis scheme for the production of polymeric pseudocrown ethers.

cyclization decreases rapidly. Winnik's group has also studied the cyclization dynamics of pyrene end-capped polystyrenes using transient fluorescence experiments. For example, researchers from Winnik's group reported the determination of cyclization rate constants from fluorescence decay data (5,6), asymmetric end-labeling of polystyrene and determination of cyclization rate constants from intramolecular exciplex emission decay data (6) and fluorescence quenching in pyrene/benzil end-labeled poly(tetramethylene oxide) (7). A review of their earlier work (8) on the cyclization of polymer chains in solution and luminescence techniques to study the morphology of prototype industrial materials, is a good source of literature in this area. Recently, Martinho *et al* (9) studied the effect of hydrostatic pressure on the cyclization of pyrene end-labeled polystyrene in various solvents and observed that the cyclization rate decreases monotonically with pressure.

Frank *et al* (10,11,12) studied the complexation of poly(acrylic acid) with pyrene-labeled poly(ethylene glycol) by monitoring the excimer-to-monomer fluorescence intensity ratio. These authors used this technique to study the hydrophobic attraction of pyrene-end-labeled polyethylene glycol in water and water-methanol

mixtures, and the effect of the hydrophobic interaction in the poly(methacrylic acid)/pyrene end-labeled poly(ethylene glycol) complexes. They also used the monomer/excimer ratio to demonstrate the effect of pH on complexes of poly(acrylic) or poly(methacrylic acid) with pyrene end-labeled poly(ethylene glycol) (13,14). Frank's group has also developed a new anionic synthesis scheme (15) for the synthesis of pyrene end-labeled polystyrene having no ester linkages. The resulting polymers demonstrated enhanced thermal and hydrolytic stability as compared to those synthesized previous methods.

The preceding two paragraphs illustrate the utility of pyrene excimer fluorescence experiments for conformation studies in cyclizing or complexing polymer systems. In this contribution, we will use this technique to investigate ion-induced cyclization of relatively short-chain oligo(ethylene glycol) molecules. We will use the monomer to excimer fluorescence ratio to characterize the extent of oligomer cyclization. Comparison of the fluorescence ratio obtained in the presence of the templating ion to that observed in the absence of the ion provides insight into the conformation of the templated ligand. Therefore, these studies serve as an experimental test of the previously reported molecular modeling results (1). In addition, we present new molecular dynamics simulations of pyrene-labeled ligands to investigate the effect of the fluorescent chromophore on the simulation results. These simulations will provide molecular insight into the fluorescence results by elucidating the effects of the templating ion and/or the pyrene end groups on the conformations adopted by the oligo(ethylene glycol) chains.

EXPERIMENTAL

Synthesis of Pyrene End-Labeled Oligomeric Ethylene Glycols

Pyrene end-labeled tetraethylene glycol (TEG) and pentaethylene glycol (PEG) were prepared based on the procedure reported by Cuniberti and Perico (2) as shown in Figure 2. 1-pyrenebutyric acid (3.11 g), was mixed with tetraethylene glycol (0.899 g) or pentaethylene glycol (1.013 g) and para-toluenesulphonic acid monohydrate (0.268 g) in a 500 ml round bottom flask equipped with a Dean Stark trap as well as a condenser. These chemicals were used as received from Aldrich. To this mixture was added 250 ml of dry toluene. The mixture was stirred and allowed to reflux overnight. The next day,

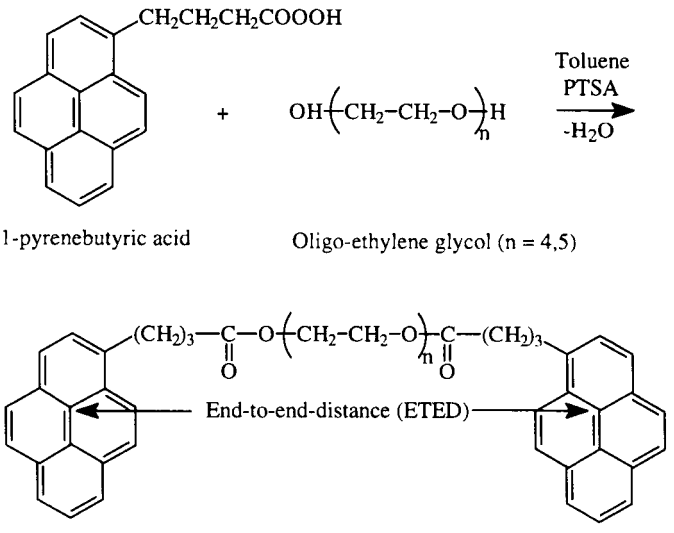

Figure 2. Scheme for synthesis of pyrene end labeled oligoethylene glycols

the reaction was stopped and TLC (silica gel) revealed one strong spot at R_f = 0.13 (hexane: ethyl acetate 1:1). The starting material, 1-pyrenebutyric acid, appears at R_f = 0.43. The product was isolated as follows. The contents of the round-bottom flask were emptied into a separatory funnel and extracted with 3 x 100 ml saturated sodium bicarbonate solution to remove the catalyst para-toluenesulphonic acid and reactants. The toluene layer was extracted once with distilled water (100 ml) and once with brine (100 ml), then stirred over anhydrous sodium sulfate for 20 minutes and filtered. Finally the solvent was evaporated on a rotary evaporator at 60°C. The dried product was placed on a high vacuum line for one hour and pumped at room temperature. The product yield was 96% and the proton and carbon-13 NMR spectra were consistent with the desired products: tetraethylene glycol and pentaethylene glycol which are pyrene-labeled on both ends (henceforth abbreviated Py-TEG-Py and Py-PEG-Py, respectively).

Fluorescence Studies

The fluorescence studies of pyrene end-labeled oligomers were performed using an Aminco-Bowman Series 2 Luminescence Spectrometer. An excitation wavelength of

322 nm was chosen based upon pyrene's absorption spectrum, and the steady-state fluorescence emission was collected for wavelengths between 330 and 630 nm. The solvent to be used for the fluorescence studies had to meet several criteria. First, it should be a solvent in which the templating ions themselves are insoluble, but are solubilized upon addition of the oligo(ethylene glycol) chains (1). This ensures that all ions in solution are bound by the oligomers, and therefore ensures maximum templatization. In addition, the solvent must meet the optical requirements of low absorption and emission in the spectral window between 300 and 630 nm. With these criteria in mind, chloroform and THF were selected for the studies. Dilute solutions of the pyrene end-labeled oligomers (Py-PEG-Py and Py-TEG-Py) were prepared in HPLC grade chloroform and THF at concentrations varying from 10^{-4} to 10^{-7} M. For studies performed in the presence of a templating ion, the cation (tin, chromium or nickel) was introduced into the polymer solution as its hydrated chloride salt (16). These salts were added in excess and the resulting solutions were agitated for 2-3 days to ensure maximum templatization and equilibration. The solutions were then filtered prior to the fluorescence studies.

Molecular Dynamics Simulations

Molecular dynamics (MD) simulations were performed on pyrene end-labeled tetraethylene glycol and pentaethylene glycol in the presence and in the absence of the templating ion. The pyrene end-labeled tetra- and pentaethylene glycols were modeled using molecular modeling software POLYGRAF (17). The molecular structures were energy minimized using the DRIEDING force field and were charge equilibrated using the Gastieger algorithm prior to the MD simulations. For simulations in the presence of the templating ion, sodium (Na^+) was introduced in proximity to the ether oxygens before energy minimization and charge equilibration. TVN MD simulations were performed in the absence of any solvent (18) at 300K for either 100 or 200 ps and their trajectories were recorded at every 0.1 ps. Our previous simulations (1) indicated that for oligomers of this relatively short chain length there is little or no effect of simulation time (above 50 ps) on the mean end-to-end distance. However, in the case of tetra- and pentaethylene glycol simulations were performed for 100 and 200 ps respectively to allow for the bulky pyrene end-groups to sample more conformations and hence provide a better average. Plots of end-to-end distance versus time were generated and plots of

energy versus time yielded almost a horizontal line thereby ensuring that all the assumed conformations were equally probable and possessed almost the same energy.

RESULTS AND DISCUSSIONS

Fluorescence Studies

Figure 3 contains fluorescence profiles of two distinct systems: a dilute solution (10^{-5} M) of 1-pyrenebutyric acid (curve A) and a similarly dilute solution (10^{-5} M) of the pyrene-end labeled oligomer Py-PEG-Py (curve B), both in chloroform. The figure illustrates that these two systems have markedly different characteristic fluorescence profiles. While both spectra exhibit sharp peaks at approximately 382 and 402 nm (characteristic of the uncomplexed, monomeric pyrene), the Py-PEG-Py exhibits a second broad peak centered at around 480 nm (characteristic of the pyrene excimer). Therefore, Figure 3 illustrates the effect of placing two pyrene molecules in proximity on the two ends of an oligomeric ethylene glycol chain. At this low concentration, the 1-pyrenebutyric acid exhibits essentially no excimer formation, indicating that the pyrene moieties all exist as uncomplexed "monomers." However, at the same low concentration, the Py-PEG-Py system exhibits significant excimer formation, indicating that pyrene moieties have formed sandwich complexes with one another. A series of studies were performed as a function of concentration to yield that, at these low concentrations, the ratio of the fluorescence intensity of the excimer peak to that of the monomer peak (the excimer-to-monomer ratio) is essentially constant, while at higher concentrations (10^{-4} M and above) this ratio exhibits an upward slope as the concentration is increased. This suggests that at low concentrations (10^{-5} M and below) the excimer formation is primarily intramolecular, with the pyrene moieties on either end of the oligomeric chain coming together to form an excimer, while at higher concentrations the intermolecular excimer formation between pyrene moieties on two different oligomers becomes significant (hence the dependence on concentration). Therefore, these studies suggest that some oligomer cyclization occurs in the pyrene end-labeled PEG even in the absence of a templating ion. This is primarily due to the fact that the oligomeric chains are rather small, leading to a locally high concentration of the two pyrene moieties attached to a single chain.

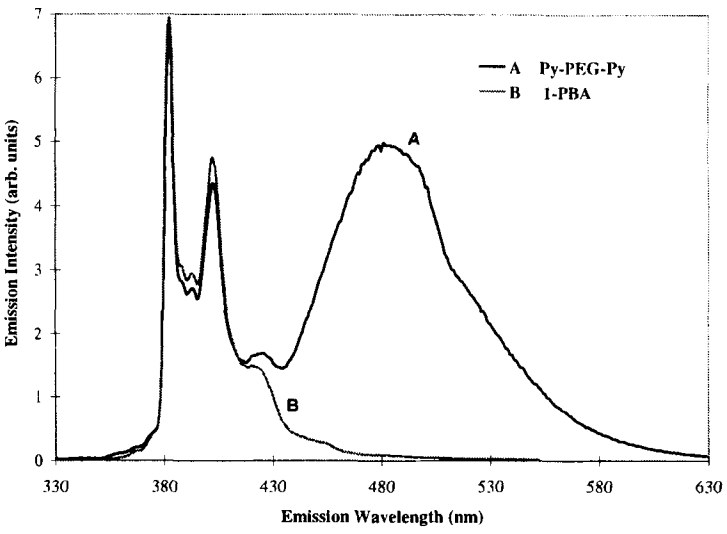

FIGURE 3. Fluorescence emission spectra of (A) pyrene end-labeled penta-ethylene glycol and (B) 1-pyrenebutyric acid. The excitation was at 322 nm and both samples were at a concentration of 10^{-5} M.

Figure 4 illustrates the effect of a templating cation on the fluorescence profile of Py-TEG-Py. The figure illustrates that in the presence of the templating ion (Ni^{2+} in this case) the fluorescence spectrum of Py-TEG-Py exhibits a significantly enhanced pyrene excimer-to-monomer ratio relative to spectrum obtained in the absence of any ion. Similar results were obtained using Sn^{2+} or Cr^{3+} as the templating ion and with chloroform as the solvent. We attribute the observed enhancement of the excimer peak upon addition of a templating cation to ion-induced cyclization of the oligo(ethylene glycol) chain. In agreement with our previous molecular modeling studies (1) these fluorescence studies indicate that the templating ion binds with the oligo(ethylene glycol) ligand, and facilitates the formation of cyclic conformations which bring the two chain ends in proximity. Similar trends were observed for the fluorescence profiles of the longer oligomeric ligand Py-PEG-Py, as shown in Figure 5.

Experimental results for the pyrene excimer-to-monomer fluorescence ratio for Py-PEG-Py in two different solvents (chloroform and THF) are illustrated in Figure 6.

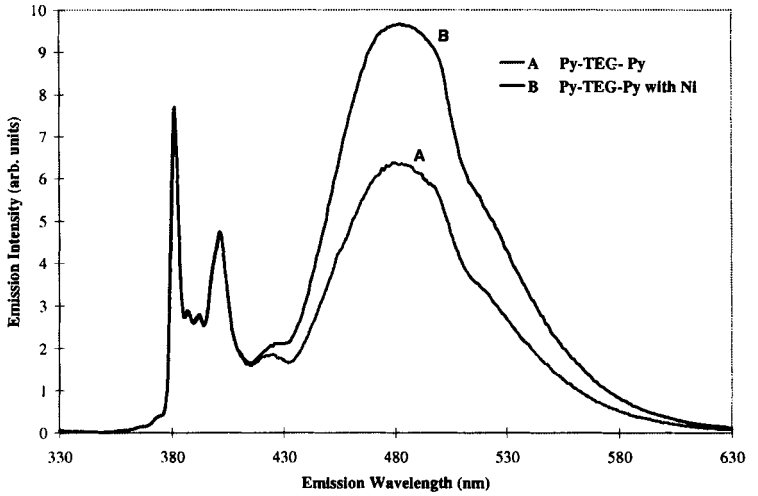

FIGURE 4. Fluorescence profiles of pyrene end-labeled tetraethylene glycol in THF solvent (10^{-5} M) in the (A) absence and (B) the presence of nickel chloride. The excitation frequency is 322 nm.

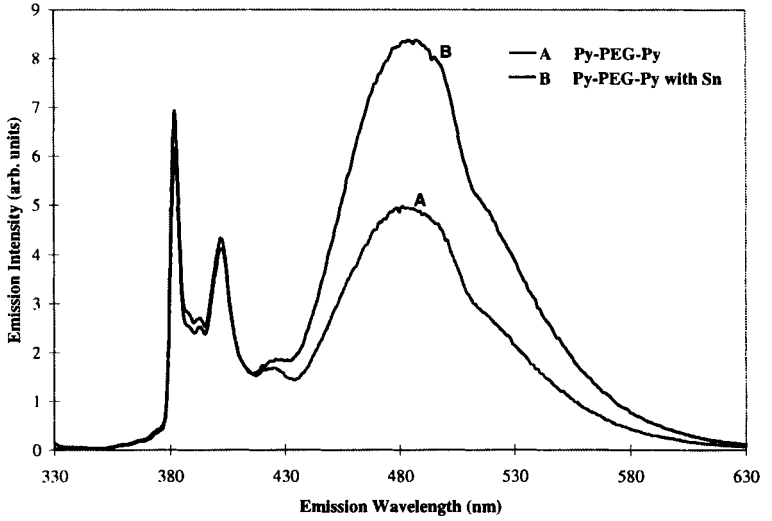

FIGURE 5. Fluorescence emission spectra of pyrene end-labeled pentaethylene glycol (10^{-5} M) in chloroform in the (A) absence and (B) presence of tin chloride. Excitation is at 322 nm.

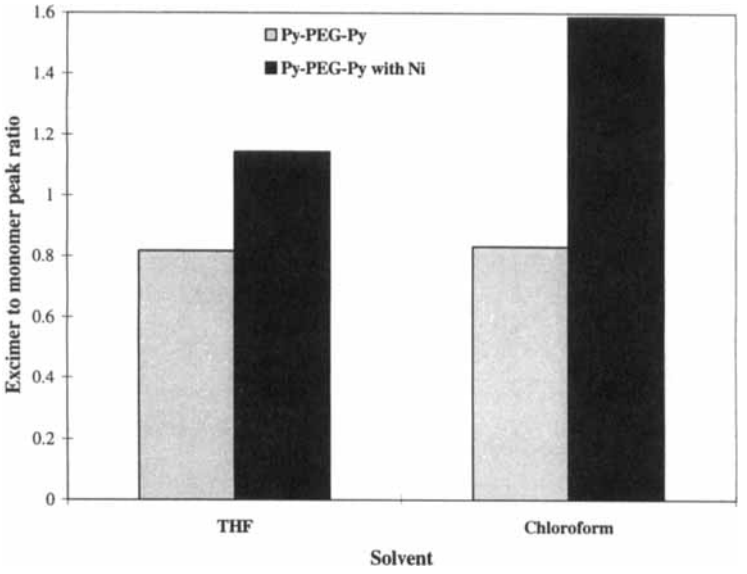

FIGURE 6. Comparison of excimer-to-monomer ratio for pyrene end-labeled pentaethylene glycol (10^{-5} M) in chloroform and THF in the presence and absence of nickel chloride.

The figure contains data obtained both in the presence and in the absence of Ni^{2+} as a templating ion for both solvents, and illustrates some interesting results. For both solvents, in the absence of the templating ion, the excimer-to-monomer ratio (I_{ex}/I_m) was found to be 0.8, suggesting the probability of cyclization was essentially the same. However, in the presence of the nickel ions the excimer-to-monomer ratio was considerably higher in chloroform than in THF. This suggests that more oligomer cyclization occurs in chloroform than THF. This result, combined with the fact that the oligo(ethylene glycol) ligands more effectively solubilize the nickel ions in chloroform (1), provides further indirect evidence for ion-induced cyclization. In addition, these studies indicate that the pyrene excimer-to-monomer fluorescence ratio provides a sensitive measure of the ability of the oligo(ethylene glycol) to solubilize the ions into an organic solvent.

Molecular Dynamic Simulations

In a previous contribution (1), we reported molecular dynamic simulations of oligo(ethylene glycol) diacrylates both in the presence and in the absence of a templating cation. These studies revealed that the addition of the templating cation leads to a significant decrease in the average end-to-end distance (in the case of tetra(ethylene glycol) diacrylate (TEGDA), the shift is from ~ 19 Å in the absence of the ion to ~ 7 Å in the presence of the ion). In the present study, molecular dynamic simulations were performed on pyrene end-labeled ligands to elucidate the effect of the large fluorescent chromophores on the chain conformations (Figure 7 and 8). These new simulations are compared to our previous simulation results in the following discussion.

Figure 9 contains simulations results for the normalized frequency distribution of the end-to-end distance for two distinct systems: pyrene end-labeled tetra(ethylene glycol), and the analogous unlabeled diacrylate (TEGDA). These results indicate that replacing the acrylate group with the pyrene chromophore results in a marked decrease in the mean end-to-end distance (ETED) while leaving the dispersion relatively unchanged (the ETED is ~19 Å for the TEGDA, and ~8.5 Å for Py-TEG-Py). These trends may be attributed to the associative interactions between two pyrene moieties (these interactions are responsible for the formation of the sandwich complex). These interactions tend to bring the chain ends in proximity, resulting in the decreased mean end-to-end distance (Figure 8). These simulation results suggest that even in the absence of a templating cation, the pyrene end-labeled oligomers exhibit an increased tendency to form cycles compared to the TEGDA. This result is consistent with the significant excimer formation even in the absence of the templating ion exhibited in Figures 3-5. Figure 10 demonstrates the further reduction in the mean end-to-end distance upon addition of the templating cation to Py-TEG-Py. The figure contains simulation results for Py-TEG-Py in the absence and in the presence of a templating ion. These molecular dynamics simulations demonstrate that the mean end-to-end distance decreases to ~5.6 Å from ~8.5 Å in the presence of the cation. Again the simulation results are consistent with the ion-induced enhancement in the excimer fluorescence shown in Figures 4 and 5.

Figure 11 demonstrates the effect of the pyrene end-labeling on the possible conformations of the templated tetra(ethylene glycol). The figure contains simulation results for both Py-TEG-Py and TEGDA in the presence of the templating ion. Figure 11

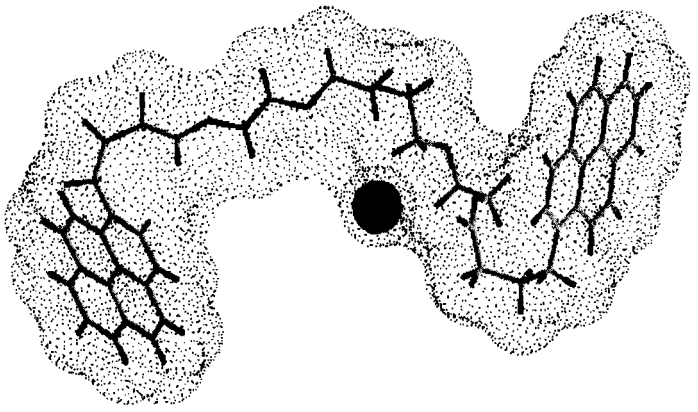

Figure 7. Starting conformation of end-labeled pentaethylene glycol in the presence of a sodium cation.

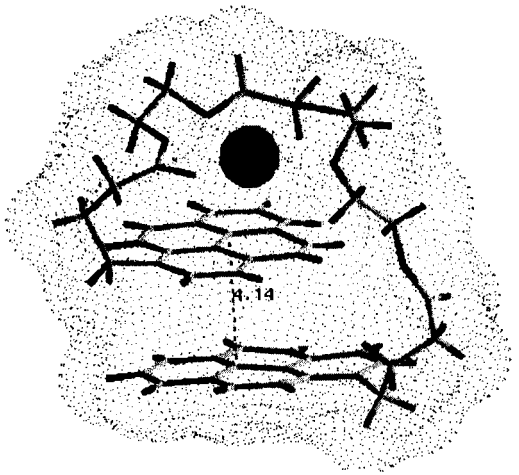

Figure 8. Pyrene end-labeled pentaethylene glycol conformation with templating cation showing pyrene excimer and the end-to-end distance (ETED).

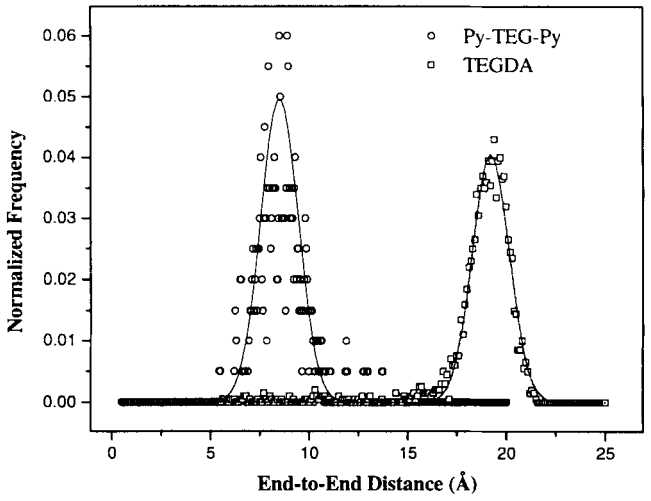

FIGURE 9. Comparison of the normalized frequency distribution of end-to-end distance for TEGDA and Py-TEG-Py demonstrating the effect of pyrene end-labeling.

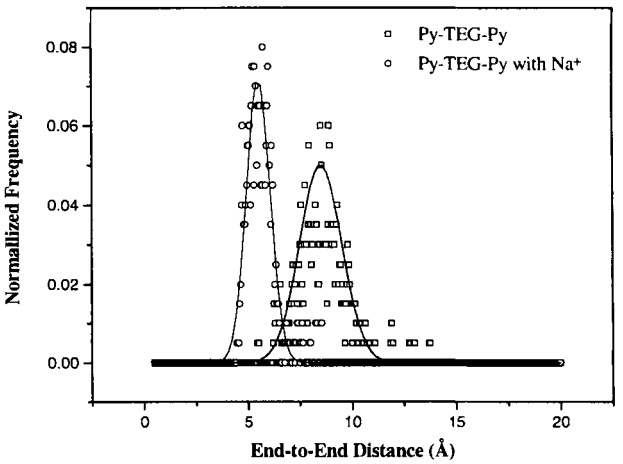

FIGURE 10. Normalized frequency distribution of end-to-end distance for pyrene end-labeled pentaethylene glycol in the presence and absence of a templating sodium cation.

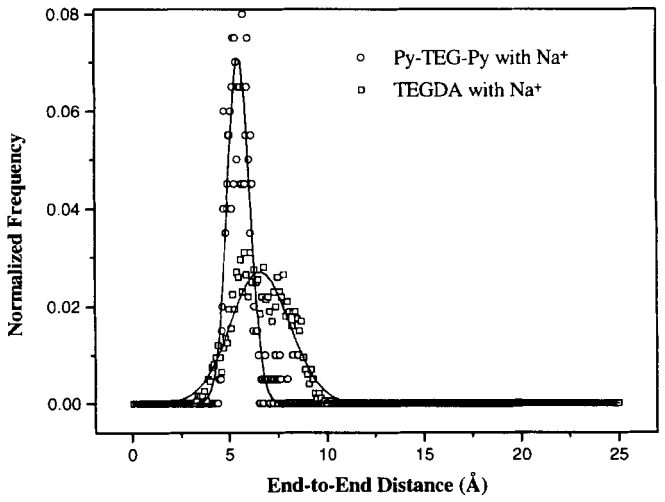

FIGURE 11. Comparison of normalized frequency distribution of end-to-end distance obtained from molecular dynamics simulations for Py-TEG-Py and TEGDA, both with a templating Na^+ cation.

once again illustrates that the templating ion greatly restricts the conformations adopted by the chain as illustrated by the reduced mean end-to-end distance compared to the ion-free simulation results shown in Figure 9. It is interesting that the simulation results suggest that while the presence of the pyrene end groups has only a slight effect on the mean value of the end-to-end distance, it has a marked impact on the dispersion. This suggests that the combined presence of the templating ion and the pyrene end groups places considerable restrictions on the conformations adopted by the oligomer.

CONCLUSIONS

In this contribution we have demonstrated the use of pyrene excimer fluorescence experiments to investigate the ion-induced cyclization of relatively short-chain, pyrene end-labeled oligo(ethylene glycol) molecules. The excimer fluorescence results demonstrated that even in the absence of any templating cation, a significant excimer emission was observed, indicating that the locally high concentration of the two pyrene moieties attached to the same oligomer leads to intramolecular cyclization. The

addition of templating cations such as Ni^{2+} and Sn^{2+} lead to further enhancements in the excimer fluorescence. These results suggest that the templating ion binds with the oligo(ethylene glycol) chain and facilitates the formation of cyclic conformations which bring the two chain ends in proximity. For pyrene end-labeled penta(ethylene glycol), the excimer fluorescence enhancement induced by nickel ions was more pronounced in chloroform than in tetrahydrofuran. Therefore the pyrene excimer-to-monomer fluorescence ratio was found to provide a sensitive measure of the ability of the oligo(ethylene glycol) mixture to solubilize the ions into an organic solvent.

Molecular dynamics simulations of pyrene-labeled oligo(ethylene glycol) ligands were performed to provide molecular insight into the fluorescence results by elucidating the effects of the templating ion and/or the pyrene end groups on the conformations adopted by the oligo(ethylene glycol) chains. Simulation results indicated that even in the absence of a templating cation, the pyrene end-labeled oligomers exhibit an enhanced tendency to form cycles compared to the analogous unlabeled ligands. This result is consistent with the fluorescence results in which significant excimer formation was observed even in the absence of any cation. Simulation results further indicated that the addition of a templating cation leads to a further reduction in the mean end-to-end distance for pyrene end labeled tetra(ethylene glycol) in a manner consistent with the observed enhanced excimer fluorescence. Finally, for two systems containing the templating ion, the presence of the pyrene end groups on the ethylene glycol oligomer has only a slight effect on the mean end-to-end distance, but leads to a marked reduction in the dispersion of the distribution. Hence, the combined presence of the templating ion and the pyrene end groups appears to place considerable restrictions on the conformations adopted by the oligomer.

The combined experiment and theoretical studies reported in this contribution provide considerable insight into the ion-induced cyclization of oligomeric ethylene glycols, and therefore enhance our understanding of the synthesis of polymeric pseudocrown ethers by the template ion method.

ACKNOWLEDGMENTS

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18. The primary reason for not including any solvent in our simulations was the fact that the solvent-cation interactions would be minimal since the cation is itself insoluble in the solvents used (chloroform and THF). Also, since in our laboratory we have solubilized salts in bulk oligoethylene glycols, the modeling may be interpreted to reflect those observations.