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ISOTHERMAL TITRATION CALORIMETRY AND TRANSMISSION ELECTRON MICROSCOPY OF MAIN-CHAIN VIologen POLYMER CONTAINING BROMIDE AS COUNTERIONS

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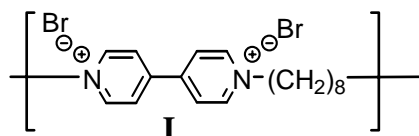
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Introduction

Polyelectrolytes are an important class of macromolecules that contain dissociable ionic groups. When introduced into polar solvent, usually the universal solvent water, dissociation takes place so that electrically charged macromolecule is suspended in solution. The electrostatic interaction is operative between ionized groups inside the macromolecule, between the macromolecules, between the counterions, and between the macromolecule and counterion. Since this interaction is characterized by its long-range nature, the solution exhibits various interesting properties including the polyelectrolyte behavior very different from solutions of neutral polymers.^{1,2} Recently, they have received resurrecting interest both for the construction of ordered solid-state structures from the interactions of various surfactants with the oppositely charged macromolecules and for the construction of functional multilayer assemblies by sequential layer-by-layer deposition technique through electrostatic interactions. These ordered-structures offer a host of interesting properties ranging from improved mechanical property to optical, electrical, and even biological properties.^{3,4} However, in contrast to the well-understanding of the structures and dynamics of neutral polymers, there is undoubtedly a lack of clear molecular interpretations for many of the fundamental properties of charged polymers. On one hand, the different theoretical treatments that are usually used to understand their various aspects include the concept of an electrostatic persistent length, counterion condensation, descriptions of entangled solution behavior, couple-mode theory, electrolytic dissipation, and phase transitions in their solutions. On the other hand, the various experimental techniques that are commonly used to decipher structures and dynamics (i.e., intrachain and interchain interactions) of this class of polymers include static and dynamic light scattering, neutron spin echo, electrical conductivity, solution viscosity, viscoelasticity, nuclear magnetic and electron spin resonance spectroscopy.^{1,2,5,6} The typical cationic polyelectrolytes that are used in various studies include poly(4-vinyl-N-alkylpyridinium), poly(4-vinylpyridine), poly(ethyleneimine), poly(vinylamine), and poly(diallyldialkylammonium). Each of them with the exception of poly(ethyleneimine) contain positively charged ions pendent to the hydrophobic polymer backbone. To date, these polyelectrolytes including anionic polyelectrolytes have been studied principally in aqueous solutions in which the hydrophobic backbones remain poorly solvated, and can promote aggregation or microphase separation because of the incompatibility of the hydrophobic backbones with water. Therefore, their various structural dynamics are related to only the long-range electrostatic interactions but also the microphase separation that generally occur in aqueous solutions.^{1,2,5,6}

In this report, we describe the characterization of a viologen polymer containing bromide as counterions by isothermal titration calorimetry (ITC) and transmission electron microscopy (TEM) techniques. The structure and designation of viologen polymer, **I**, which was used in this study, are shown below.



Experimental Section

Monomers. The 4,4'-bipyridyl was purchased from Sigma-Aldrich Chemical Co. and purified by recrystallization twice from toluene. The 1,8-dibromooctane was also purchased from Sigma-Aldrich and distilled under reduced pressure before use.

Polymer Synthesis. Equimolar amounts of 4,4'-bipyridyl and 1,8-

dibromooctane were reacted under stirring in N,N-dimethylformamide (DMF) at 80 °C for 72 h. A partial precipitation occurred during the polymerization reaction. At the end of polymerization reaction, the reaction flask was cooled to room temperature, and the polymer was precipitated out completely with the addition of ethyl acetate. It was filtered immediately, dried in vacuum for 24 h and stored in a desiccator.⁷ It was characterized by FTIR, FT-NMR and elemental analysis. Anal. Calcd for C₁₈H₂₄N₂Br₂ (**I**): C, 50.49; H, 5.65; N, 6.54; Br, 37.32. Found: C, 51.22; H, 5.82; N, 7.06; Br, 35.75. Its measured inherent viscosity in methanol at 35 °C was 0.46 dL/g at a polymer concentration of 0.2 g/dL. It exhibited a biphasic liquid-crystalline solution at a concentration of 39 wt % and a lyotropic solution at concentration of 51 wt % in water, respectively.

Microcalorimetry. Isothermal titration calorimetry (ITC) is a technique that measures the released or absorbed heat upon mixing of two solutions. The instrument used in this work is a VP-ITC microcalorimeter from Calorimetry Sciences Corporation (Lindon, UT). Two identical spherical cells, a reference cell and a sample cell both with a volume of 1.30 mL, are enclosed in an adiabatic jacket. The working cell is filled with the sample solution, and the reference cell is filled the solvent water used to prepare the sample solution. The titrant is injected stepwise into working cell with a syringe of total volume of 250 μ L. The sample cell is constantly stirred. For the experiments reported here the stirring rate was 310 rpm. The measurement is performed at constant temperature of 25 °C. Small aliquots of titrant (typically 20 μ L) are successively injected into the solution of working cell. The first injection is usually set to a volume of 20 μ L. Because of possible dilution during the equilibration time preceding the measurement, the first injection was ignored in the analysis of the data. Each injection produces a characteristic peak in the heat flow (J/s) due to released or absorbed heat. In the analysis, a baseline is subsequently subtracted from the data. It corresponds to the signal between consecutive injections when no change in the heat flow is detected. An exothermic reaction yields a negative peak signal because of the released heat in the sample cell is no longer required from the resistive heater of the instrument. Similarly, an endothermic reaction causes a positive peak. Integrating each of the peaks provides the heat per injection. The data analysis was performed using the software provided by Calorimetry Sciences Corporation.

Transmission Electron Microscopy. The samples for transmission electron microscopy were prepared by an adsorption technique. Droplets of a specific concentration of polymer **I** solution in water were put on 400-mesh carbon-coated copper grids. After 1 min of adsorption time, the excess solution was removed from the carbon film. Dried samples were studied with an energy filter transmission electron microscope (Tecnai G2 F30 S-TWIN) at an accelerating voltage 300 kV.

Results and Discussion

Figure 1A shows the heat per injection obtained from integrating the heat flow from raw ITC data (not shown) when water (20 μ L/injection) was injected into a 104 mM concentration of polymer **I** solution (1.30 mL) in the working cell; and Figure 1B shows heat per injection as a function of polymer **I** concentrations in the working cell. It is important to note here that in the course of a dilution measurement the polymer **I** concentration decreases in the working cell and, therefore, the slope of the heat dependent in Figure 1B is inverted when compared with the Figure 1A. Similarly, three other separate dilute experiments of polymer **I** concentrations of 50, 25, and 12 mM were performed under identical conditions, but their plots are not shown. However, all of these dilution experiments suggest that the dilution of polymer **I** with water is endothermic over the whole examined concentrations and the magnitude of the signal decreases with the decrease in polymer concentration. Attempts to unveil the cross-over to the exothermic signal with the further lower concentration of polymer **I** failed because of the detection limit of the instrument. Although polyelectrolytes both rigid-rod and flexible types are becoming an interesting class of materials, but their solution properties by ITC measurements are relatively rare.⁸ Sinn *et al.* reported the dilution experiments of poly(sodium acrylate), NaPAA, and poly(sodium styrenesulfonate), NaPSS, with water over a broad range of concentrations were studied by ITC and compared to the corresponding low molecular salts, sodium acetate, NaAc and sodium sulfate. Interestingly enough, NaPAA is only weakly exothermic and shows nearly ideal behavior over the whole examined range up to 1 M solutions. Its heat of dilution depends weakly on its molecular weights. In contrast, the dilution of NaAc is exothermic over the whole examined range of concentrations. The magnitude of the signal increases with concentration.

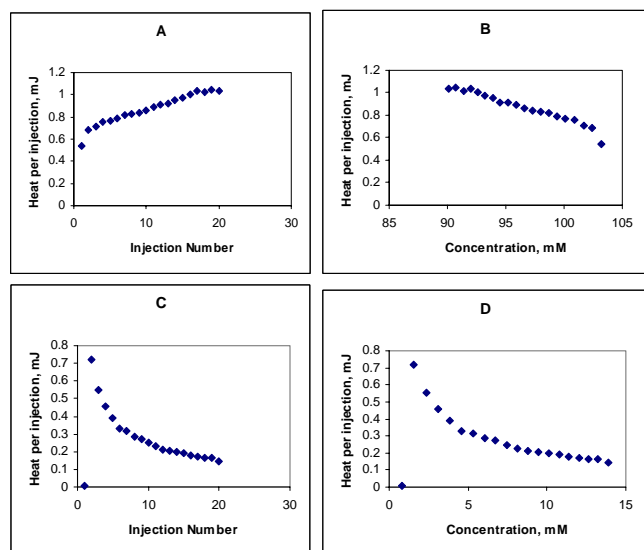


Figure 1. (A) Heat per injection obtained from integrating the heat flow over time (from raw ITC data) when water (20 $\mu\text{L}/\text{injection}$) was injected into a 104 mM polymer I solution in the working cell ; (B) Heat per injection as a function of polymer I concentrations in the working cell; (C) Heat per injection obtained from integrating the heat flow over time (from raw ITC data) when 104 mM polymer I solution (20 $\mu\text{L}/\text{injection}$) was injected into water in the working cell ; and (D) Heat per injection as a function of polymer I concentrations in the working cell.

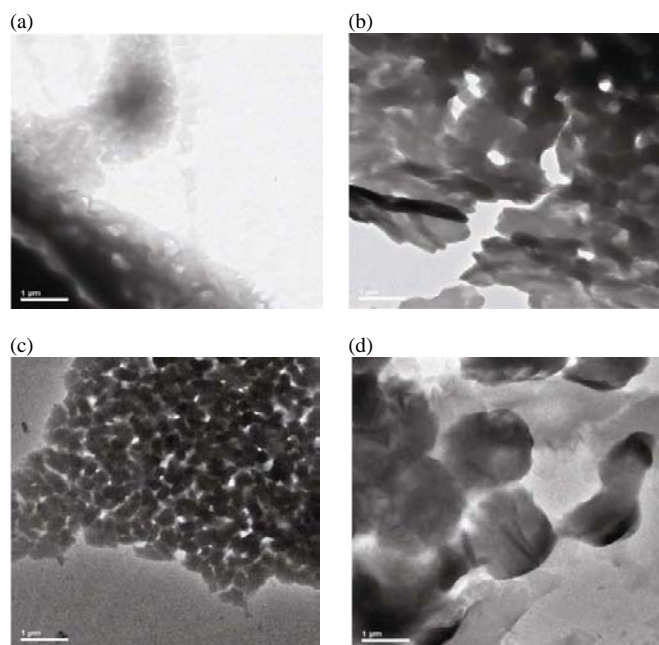


Figure 2. TEM micrographs obtained at increasing concentrations of polymer I solution in water (a) 1.13 (b) 4.4 (c) 10 and (d) 50 wt % displaying gradual aggregation and overlapping aggregated structure leading to spheroids morphology (magnification 5600 \times).

The released heat suggests that there exists a local exothermic binding and rearrangement of water molecules around the acetate anion. The dilution experiments of NaPSS suggest that it is exothermic at low concentrations and turns only slightly endothermic at high concentrations. On the contrary, sodium sulfate exhibits a slight exothermic at low concentrations, but highly endothermic at high concentrations. The strikingly similar heats of dilution data of NaPAA and NaPSS obtained by ITC were quite surprising, despite they differ significantly in their chemical structures and in the polarizability of

their charges. Note here that both the polymers contain the charged groups as pendent groups attached to the flexible polymer chains. However, polymer I is a main-chain ionic polymer having octamethylene units as hydrophobic moieties, which interacts with water apparently in a different manner leading to the endothermic process with dilution.

Figure 1C shows the heat per injection obtained from integrating the heat flow over time (from raw ITC data) when 104 mM polymer I solution (20 $\mu\text{L}/\text{injection}$) was injected into water in the working cell and Figure 1D shows the heat per injection as a function of polymer I concentrations in the working cell. Similarly, three other separate experiments of polymer I concentrations of 50, 25, and 12 mM were also performed under identical conditions, but their plots are not shown. Note here that this set of experiments also suggest that the interaction of polymer I with water is also endothermic over the whole examined concentrations and the magnitude of the signal also decreases with the decrease in polymer concentrations. Note here that, unlike Figures 1A and 1B, in this set of experimental conditions, the slope of the heat dependent remained essentially identical, since the concentration of polymer increases in the working cell with the successive injections of polymer solutions.

Figure 2 shows TEM micrographs of polymer I obtained from various range of concentrations from 1.13 to 50 wt % in water. It is evident from these micrographs that even at low concentration it exhibits an aggregated structure, which then develops with the further increase in polymer concentrations to spheroids morphology. This polymer also exhibited a lyotropic solution at 51 wt % in water.⁹ The aggregation phenomena of ionic polymers irrespective of the nature of polyions (rigid-rod or flexible) are quite remarkable in general, since the macroions approach one another leading to the formation of aggregates instead of repulsion between like charges. The mechanism of this aggregation process remains unknown to date, but aggregation processes do occur in both flexible and rod-like polyelectrolytes as detected by various experimental techniques. For example, aggregation of flexible NaPSS in water was detected by light microscopy and dynamic and static light-scattering.¹⁰ The dimensions of these aggregates increase with the increase in polymer concentration and molar mass of polymer. Similar aggregation phenomena were also detected in the rigid-rod ionic polymers of carboxylated poly(phenylene ethylene) and sulfonated poly(para-phenylene) in water by dynamic and static light-scattering, small-angle X-ray scattering, scanning force microscopy and TEM.^{11,12}

Conclusions

Dilution experiments of main-chain viologen polymer containing bromide as counterions by ITC technique suggested that the interaction of this polymer with water is endothermic, unlike polymers NaPAA and NaPSS. This result may be related to the difference mechanism of hydration of ionic groups in the main chain. It also underwent different levels of aggregation in water producing spheroids morphology with the increase in high polymer concentrations.

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