Counterion Dissociation Dependence of Chain Conformation for Poly(xylylene tetrahydrothiophenium chloride) in Semidilute Aqueous Solution

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Introduction

The polyelectrolyte solutions show an anomalous behavior in semidilute salt-free systems or with low salt content, in that the reduced viscosity η_{red} is abruptly increased with decreasing segmental concentration c_p. Such phenomenon was first reported by Fuoss and Strauss in 1948,[1] who described it with an empirical equation: $\eta_{red} = A/(1+Bc_p^{1/2})$, where A and B are constants. In 1976, de Gennes et al.[2] derived a similar expression $\eta_{red} \sim c_p^{-1/2}$, by assuming that the polyelectrolyte chains are in a rigid rod conformation. However, most of the experimental data[3−5] did not support the scaling relation of $\eta_{red} \sim c_p^{-1/2}$. Recently, we have suggested the polyelectrolytes as a flexible chain with the end-to-end distance $R = N^{\nu}a$, where N is the number of mers in a chain, a is the length per mer and ν is the chain conformation index, and used the scaling relation of $\eta_{red} \sim c_p^n$ to derive the following expression[6]

$$\nu = \frac{n+2}{3n+3} \qquad (1)$$

Accordingly, the exponent n changes from −0.5 for a rodlike chain conformation ($\nu = 1$) to 1 for a Gaussian flexible chain ($\nu = 0.5$).

Poly(xylylene tetrahydrothiophenium chloride) (PXT) is a polyelectrolyte and known as a polymer precursor of poly(phenylenevinylene), which is the first reported polymer possessing electroluminescence.[7] The obtained new scaling relation was able to estimate the chain conformations of PXT in the semidilute regime with and without containing external salts, simply by calculating n from the double-logarithmic plots of reduced viscosity vs concentration.[6] We have also demostrated that the new scaling relation could correct the deviation of linear relationship of η_{red} with the molecular weight of PXT at constant c_p.[8]

The conformation of PXT in aqueous solution is mainly influenced by the dissociation extent of counterions. Although the conductivity of polyelectrolyte solutions can provide some measure of counterion dissociation,[9] the interpretation for the conductivity measurements of polyelectrolyte solutions has relied primarily on Manning's conductivity theories.[10,11] However, it is still in doubt if they were able to apply to the semidilute regime because of overlapping of the polymer chains. Kuhn et al.[12] has suggested that Manning's theory underestimates the number of condensed counterions in the semidilute regime. We have also found that the extent of aggregation of polyelectrolytes in the semidi-

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lute salt-free aqueous solution substantially affects the ionic conductivity of the solution.[13]

In our previous study on the counterion dissociation of PXT in the salt-free semidilute aqueous solution, we have modified Manning's conductivity theory by allowing the dissociation extent f of counterions adjustable to fit the experimental data of equivalent conductivities Λ shown as below[8]

$$\Lambda = f(\lambda_c^o + \lambda_p) \qquad (2)$$

where λ_c^o is the equivalent conductivity of the counterion in water and λ_p is the equivalent conductivity of the polyions in the aqueous solution, given by

$$\lambda_p = \frac{279A|z_c|^{-1} \ln \kappa r}{1 + 43.2(|z_c|\lambda_c^o)^{-1}A \ln \kappa r} \qquad (3)$$

where

$$A = \frac{\epsilon KT}{3\pi\eta e} \qquad (4)$$

r is the radius of the polyions and κ is the Debye−Hückel screening constant

$$\kappa^2 = \left(\frac{4\pi e^2}{\epsilon KT}\right)\frac{c_p}{\xi_M} \qquad (5)$$

where e is the electronic charge, ϵ is the dielectric constant of water and ξ_M is the charge density parameter, i.e.

$$\xi_M = \frac{Q}{b} = \frac{e^2}{\epsilon KTb} > |z_c|^{-1} \qquad (6)$$

where z_c is the valence of the counterion, $Q = e^2/\epsilon KT$ is the Bjerrum length, and b is the charge spacing of the polyelectrolyte chain. As a result, the obtained f was decreased with the polymer chain length and much lower than the theoretical value f_{theo} calculated by[10]

$$f_{theor} = 0.886|z_c|^{-1}\xi_M^{-1} \qquad (7)$$

The deviation of f from f_{theor} which is invariant of molecular weight was considered to result from the overlapping of polyelectrolyte chains in the semidilute solution influencing the counterion dissociation.

In this study sodium chloride external salt was employed to further reduce the counterion dissociation from PXT in the aqueous solution. With f estimated by the modified Manning theory, in particular for the salt-containing polyelectrolyte[11] and ν estimated from the plots of reduced viscosity vs segmental concentration, the relationship between ν and f was then established.

Experimental Section

The PXT with a number-average molecular weight of 365 000 and a dispersity of 3.2 was prepared via a sulfonium precursor route.[14] The detail description of molecular weight determination was given elsewere.[6] The PXT aqueous solutions were prepared from the volumetric dilutions for concentrations ranging from 0.015 to 0.00002 g/dL, respectively. Polymer
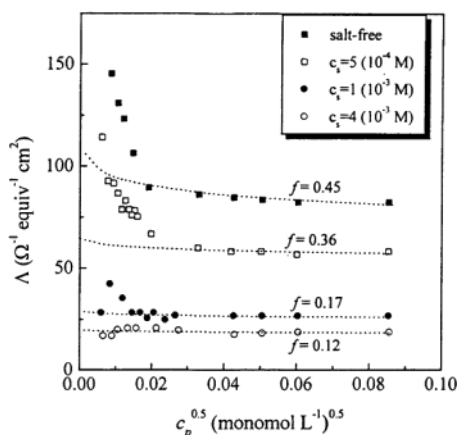
Figure 1. Concentration dependence of equivalent conductivities of PXT in salt-free and NaCl salt-containing aqueous solutions at indicated c_s. Note: the curve on the data points was drawn from eq 2 with f adjusted to fit the data.

solutions with added sodium chloride (NaCl) salts were prepared from the highest polymer concentration first and then gradually diluted with sodium chloride aqueous solutions having predetermined concentrations.

The viscosity measurements were carried out by using a capillary Ubbelohde viscometer (type 0A, Cannon Co.) immersed in a thermostat water bath (TAMSON Co., model TV 2000) maintained at 30 ± 0.01 °C. A typical flow time of polymer solutions in a viscometer was measured in a range of 100−300 s with an accuracy of ±0.1 s, and each flow time was determined by repeating at least five time measurements. The conductivity measurements were conducted in a beaker containing 100 mL polymer solutions at 30 ± 0.01 °C under a nitrogen atmosphere, by using a conductivity cell, with platinized electrodes and a cell constant of 3.64 cm^{-1}. The signal was recorded on a Radiometer Copenhagen CDC-230 conductivity meter, and the data were then subtracted by the conductivities of water and NaCl external salts.

Results and Discussion

Figure 1 shows the plots of equivalent conductivity of PXT in salt-free and NaCl salt containing aqueous solutions vs $c_p^{0.5}$. For the salt-free aqueous solution, we have used eqs 3−6 to calcuate λ_p and eq 2 to fit the experimental data by giving $f = 0.45$ in our previous study.[8] For the salt-containing solutions, the other Manning theory particularly applied to the salt-containing polyelectrolyte solutions[11] was employed to calculate λ_p, that is

$$\lambda_p = U \tag{8}$$

where U is the electrophoretic mobility of polyelectrolyte chains, expressed by
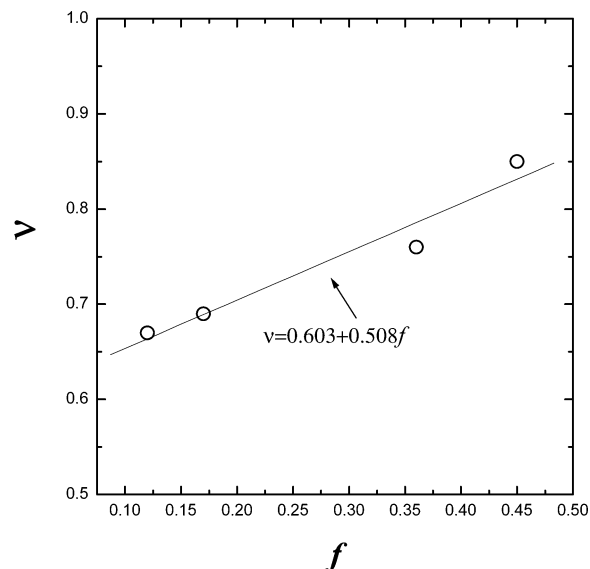
$$300U = (300U^*)(\alpha/\beta) \tag{9}$$

in that $300U^*$ contains only the charged-solvent effect and was given by

$$300U^* = |z_1|^{-1}[\epsilon kT/(3\pi\eta e)]|\ln(kb)| \tag{10}$$

while

$$\alpha = 1 - {}^1/_3\nu_1(\nu_1 + \nu_2)^{-1}|z_1z_2|^{-1}(z_1^2 - z_2^2) \tag{11}$$

$$\beta = 1 + 108\nu_1(\nu_1 + \nu_2)^{-1}(300U^*)\left(\frac{z_1^2}{\lambda_1{}^s} + \frac{z_2^2}{\lambda_2{}^s}\right) \tag{12}$$

Figure 2. Plot of the chain conformation index ν vs the dissociation extent f of counterions of PXT. Note: the line with linear equation was obtained by fitting the data with the first-order least-squares method.

where ν_i is the number of ions of species i in the formula for the small electrolyte (e.g., $\nu_1 = 1$, $\nu_2 = 1$ for NaCl). $\lambda_i{}^s$ is the ionic conductivity of the small ions, z_i is the valence of the small ions, and κ defined here is as follows:

$$\kappa^2 = \left(\frac{4\pi e^2}{\epsilon KT}\right)\left(\frac{c_p}{\xi_M} + 2c_s\right) \tag{13}$$

Equations 8−13 were used to calculate λ_p as a function of c_p in various c_s. f was then obtained by fitting the experimental data in Figure 1 with calculated λ_p substituting for eq 2. The results indicated that f was decreased with the concentration of NaCl external salts. Since f is also an indication of chain conformations of PXT in the semidilute regime, we plotted the conformation index ν obtained from ref 6 as a function of f. The results shown in Figure 2 indicate that they could be fit by the first-order least-squares method with the following relationship:

$$\nu = 0.603 + 0.508f \tag{14}$$

ν closes to 0.6 at $f \rightarrow 0$, which is agreeable with most of the theoretical predictions.[15,16] Rubinstein et al.[15] have pointed out that, for the polyelectrolyte solutions in the semidilute regime with high salt content to screen the Coulomb interaction between charged monomers, the concentration dependence of the correlation length ξ is similar to that of the uncharged polymer $\xi \sim c_p^{-0.75}$, which is corresponding to $\nu = 0.6$ according to our scaling relation.[6] A similar result was also obtained by Muthukumar,[16] who gave $n = 0.25$ in $\eta_{red} \sim c_p{}^n$ for the polyelectrolyte solutions with high salt content, which is also corresponding to $\nu = 0.6$ by substituting it for eq 1.

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