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Langmuir, 2002, 18 (20), 7287-7290 • DOI: 10.1021/la011858k

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Molecular Weight Dependence of Chain Conformation and Counterion Dissociation of Poly(xylylene tetrahydrothiophenium chloride) in the Salt-Free **Semidilute Aqueous Solutions**

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Received December 28, 2001. In Final Form: July 3, 2002

The chain conformations of poly(xylylene tetrahydrothiophenium chloride) (PXT) in the salt-free semidilute aqueous solutions, estimated from the double-logarithmic plots of reduced viscosity vs segmental concentrations, were found to be more extended when the molecular weight or chain length was decreased. The dissociation extent of counterions from the PXT chains estimated from the ionic conductivity measurements was also increased. Besides, when the molecular weight was over 150 000 g/mol, the chain conformations were influenced more by the chain length than the counterion dissociation.

Introduction

Poly(xylylene tetrahydrothiophenium chloride) (PXT) with a chemical structure of



is known as a polymer precursor of poly(phenylenevinylene) (PPV), which is the first reported polymer possessing electroluminescent properties.¹ Because PPV is insoluble and intractable, the PPV films were usually prepared by casting the PXT solution and followed by baking to remove the tetrahydrothiophene side groups. Thus, the properties of resulting PPV are greatly affected by the solution behavior of PXT. In our previous study, we have derived a scaling relation to estimate the chain conformations of PXT in salt-free and salt-containing aqueous solutions, simply by using the double-logarithmic plots of reduced viscosity vs segmental concentrations.²

In general, the polyelectrolyte aqueous solutions in the semidilute regime show an anomalous behavior that the reduced viscosity $\eta_{red} = \eta - \eta_0 / \eta_0 c_p$ abruptly increased with decreasing the segmental concentration $c_{\rm p}$, where η is the viscosity of polyelectrolyte solutions and η_0 is the viscosity of solvent. Such a phenomenon was first reported by Fuoss and Strauss in 1948,3 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.⁴ derived a similar expression, $\eta_{
m red} \sim c_{
m p}^{-1/2}$, with an assumption that the polyelectrolytes are in a rodlike conformation. However, most of the reported experimental data 5^{-7} and recent theoretical studies⁸⁻¹⁰ did not support the above relation, and neither supports the notion of rodlike chains in the semidilute regime. Therefore, we treated the polyelectrolytes as a

flexible chain, that is, a succession of segmental sections (or blobs), each of which carries a gnumber of monomers.² On the basis of Rouse dynamics, the viscosity of polyelectrolyte solutions in the semidilute regime was expressed by11

$$\eta - \eta_0 = \frac{1}{36} \rho \overline{r_0}^2 N^* f_0 \tag{1}$$

where ρ = moles of polymer chains/volume $\approx c_p/N$, *N* is the number of segments per chain, $\overline{r_0}^2 = N^* \xi^2$ is the mean-square end-to-end distance of a single chain, ξ is the blob size, $N^* = N/g$ is the number of blobs per chain, $f_0 = 3\pi\eta_0\xi$ is the friction coefficient for one blob against the solvent, and $g \approx c_{\rm p} \xi^3$, indicating that the mesh size in the solution is equal to the blob size. Accordingly, eq 1 was rewritten as follows:2

$$\eta_{\rm red} = \frac{\eta - \eta_0}{\eta_0 c_{\rm p}} \approx \frac{N}{c_{\rm p}^{2} \xi^3} \tag{2}$$

Because of the overlapping of polymer chains and the formation of an isotropic network in the semidilute regime, all properties of the polymer solutions lose their molecular mass dependence. Thus, the behavior of the polymer solutions is governed by the blob size that is a function of segmental concentration but independent of polymeric molecular weight. By using the formula of correlation length provided by de Gennes et al.,⁴

$$\xi = R \left(\frac{c^*}{c_p}\right)^m \quad (c_p \gg c^*) \tag{3}$$

where $c^* \sim N R^3$ is the critical concentration that divides the dilute and the semidilute regimes and $R = N^{\nu}a$ is the end-to-end distance of the chains, we obtained $\xi \approx N^{\nu+m-3\nu m}c_{\rm p}^{-m}$. Since $\xi \approx N^0$, $m = \nu/(3\nu - 1)$. From eq 2 and the $\eta_{\rm red} \approx c_p^n$ expression, we obtained²

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$$n = -\left(\frac{3\nu - 2}{3\nu - 1}\right)$$
 or $\nu = \frac{n+2}{3n+3}$ (4)

It can be found that the exponent *n* changes from $-\frac{1}{2}$ for a rodlike chain conformation ($\nu = 1$) to 1 for a Gaussian flexible chain ($\nu = 0.5$). For a real free-coil chain ($\nu = 0.6$), n = 0.25 was obtained. A similar result was also obtained by Muthukumar,¹² who gave n = 0.25 for the polyelectrolyte solutions with high salt content. The obtained scaling relation was able to estimate the chain conformations of polyelectrolytes in the semidilute regime simply by calculating *n* from the double-logarithmic plots of reduced viscosity vs segmental concentration.²

In this study, the PXT samples with various molecular weights were prepared, and their chain conformations in the salt-free semidilute aqueous solution were estimated from eq 4. The results were then associated with the dissociation extent of counterions from the PXT chains. The latter were estimated from the ionic conductivity measurements on the basis of the modified Manning's conductivity theories¹³ by considering the influence of chain overlapping in the semidilute regime.

Experimental Section

Materials. The PXT with various molecular weights were prepared via a sulfonium precursor route using p-xylylene-bis-(tetrahydrothiophenium chloride) monomer, which was synthesized as follows:¹⁴ 10 g of dichloro-*p*-xylene (Tokyo Kasei) was dissolved in 150 mL of methanol, and then 10 mL of tetrahydrothiophene (Janssen Chimica) was added to react. After they were reacted at 50 °C for 20 h, the solution was concentrated, and 250 mL of cold acetone was added to precipitate the monomer. A white monomer crystalline was obtained after filtration, washing with cold acetone several times, and drying. The polymerization was carried out as follows: 0.4 M monomer aqueous solution (20 mL) was mixed with 80 mL of pentane and then cooled to 0 °C. Various concentrations of 0 °C, 20 mL sodium hydroxide (NaOH) aqueous solution were added into the solution under nitrogen. After polymerization for 1 h, the reaction was terminated with 0.1 M HCl to pH 7. The NaOH concentrations ranging from 0.1 to 0.4 M was used to prepare four polymer samples: PXT(I), PXT(II), PXT(III), and PXT(IV) with decreasing molecular weight, as listed in Table 1. The prepared PXT solutions after removing pentane with separation funnel were dialyzed in a membrane tube (molecular weight cutoff: 3500 g/mol) against deionized water for at least a week. At this stage, the sodium ion content remained at \sim 3 ppm, which was measured by using a GBC 902 model atomic analyzer.

Methods. To overcome the inherent problems in determining the molecular weight of polyeletcrolytes, we have replaced the ionic moieties of PXT with neutral thiophenolate groups by following ref 15. The molecular weights and molecular weight distributions were then measured by gel permeation chromatography (Testhigh series III pump and model 500 UV detector with THF as a mobile phase). The calibration curve was obtained from the monodispersed polystyrene standard sample. Water used to prepare the aqueous solution was purified by the Barnstead Easypure RF system to a resistivity of 18.3 MQ·cm. The solutions were then prepared by volumetric dilutions for concentrations ranging from 0.15 to 0.0002 g/dL. The viscosity measurements were carried out by using a capillary Ubbelohde viscometer (type 0A, Cannon Co.) immersed in a thermostatic water bath (TÅMSON Co., model TV 2000) maintained at 30 \pm 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 ± 0.01 s, and each flow time was determined by repeating at least five measurements. The conductivity measurements were conducted in a beaker containing 100 mL of polymer solutions at 30 ± 0.01



Figure 1. Double-logarithmic plots of (a) specific viscosity and (b) reduced viscosity (dL/g) vs segmental concentration (g/dL) of PXT(I) in salt-free aqueous solutions. The numbers denote the slopes of lines in different regimes of concentrations.

Table 1. Molecular Weight Data of Prepared PXT Samples

sample	$ar{M}_{ m n}$, g/mol	$ar{M}_{ m w}$, g/mol	$ar{M}_{ m w}/ar{M}_{ m n}$
PXT(I)	365 000	1 170 000	3.2
PXT(II)	154 000	430 000	2.8
PXT(III)	93 000	140 000	1.5
PXT(IV)	25 000	100 000	4.0

°C under nitrogen by using a conductivity cell with a cell constant of 3.64 cm⁻¹. The signal was recorded on a Radiometer Copenhagen CDC-230 conductivity meter, and the data after subtracting the conductivity of water were used.

Results and Discussion

Chain Conformations in the Semidilute Regime. Parts a and b of Figure 1 show the double-logarithmic plots of specific viscosity $\eta_s = (\eta - \eta_0)/\eta_0$ and reduced viscosity η_{red} , respectively, vs the PXT(I) concentration in aqueous solutions. Three regimes with different slopes are clearly seen from the plots in Figure 1b. According to Muthukumar,12 the chain behavior of polyelectrolytes in the dilute regime that $\eta_{\rm red}$ increased with $c_{\rm p}$ can be described by Zimm dynamics.¹⁶ When the concentration was increased to semidilute regime, the polymer chains began to overlap with each other and then melt into an isotropic lattice. Because the chain entanglement effect was not taken into account in the semidilute regime, the behavior that η_{red} decreased with c_p can be described by Rouse dynamics.¹¹ When the concentration was further increased to the chain entanglement regime, $\eta_{\rm red}$ turned

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Figure 2. Double-logarithmic plots of reduced viscosity vs segmental concentration of PXT with various number-averaged molecular weights in salt-free aqueous solutions; $M_n = (\blacksquare)$ 365 000, (□) 154 000, (●) 93 000, and (○) 25 000 g/mol. The lines with indicated slopes were obtained by fitting the data with the first-order least-squares method.



Figure 3. Plots of the chain conformation index ν and the dissociation extent of counterions fof PXT in semidilute aqueous solutions vs the number-averaged molecular weight.

to increase with $c_{\rm p}$ again and can be described by the reptation dynamics.¹⁷ Thus, on the basis of Muthukumar's arguments,¹² we were easy to determine the semidilute regime of PXT(I) aqueous solution to be between c^* and $c_{\rm e}$ as indicated in the figures. By using the slope of doublelogarithmic plot of reduced viscosity η_{red} vs c_p to calculate the conformation index of PXT(I) from eq 4, we obtained $\nu = 0.85$ and R = 3406 Å.

When the molecular weight of PXT was decreased, the reduced viscosity at the same segmental concentration was also decreased as shown in Figure 2. However, the slope of double-logarithmic plot of $\eta_{\rm red}$ vs $c_{\rm p}$ in the semidilute regime was increased. Again, by using eq 4 to calculate the conformation indexes, the results shown in Figure 3 indicate that the PXT chains were more extended when the molecular weight was decreased. The tendency is agreeable with most of the theoretical predictions for polyelectrolytes.^{8,18,19} Since $\eta_{red} \approx Nc_p^n$, we plotted the reduced viscosity of PXT in various concentrations vs



Figure 4. Reduced viscosity of PXT in salt-free aqueous solutions as a function of number-averaged molecular weight for various segmental concentrations.



Figure 5. $\eta_{red}/c_p{}^n$ of PXT with various segmental concentrations in salt-free aqueous solutions as a function of number-averaged molecular weight; $c_p = (\blacksquare) 0.003$, (O) 0.004, (\Box) 0.006, and (\bigcirc) 0.008 g/dL.

molecular weight as shown in Figure 4. As seen in the figure, linear dependence of $\eta_{\rm red}$ on the molecular weight was only applied up to $M_{\rm n} = 154\ 000\ {\rm g/mol.}$ Deviations from linearity were observed for the highest molecular weight. Similar results were also reported by Cohen et al.²⁰ for the poly(sodium styrenesulfonate) in aqueous solutions. They implied that the deviation might be due to the shear thinning effect. However, according to our experimental results shown in Figure 3, the slope *n* in the double-logarithmic plot of reduced viscosity η_{red} vs c_p was dependent on the molecular weight. If we plotted $\eta_{\rm red}/c_{\rm p}{}^n$ vs the molecular weight, all the data were merged into a single line as shown in Figure 5. Apparently, the deviation from the linear relations for the highest molecular weight shown in Figure 4 was not due to the shear thinning effect but due to the less extended chain conformation.

Counterion Dissociation. Figure 6 shows the equivalent conductivities of PXT(I) aqueous solutions as a function of the square root of segmental concentration $c_p^{1/2}$ in mol^{1/2} L^{-1/2}. They were barely changed with decreasing the segmental concentration until c^* was

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Figure 6. Equivalent conductivities of PXT(I) as a function of square root of segmental concentrations. Note: the curves above the data points were drawn from eq 5 with f_{theo} , whereas those on the data points were drawn with f.

reached and then increased rapidly. According to the Manning's conductivity theory for salt-free polyelectrolyte solutions, 13,21

$$\Lambda = f_{\text{theo}}(\lambda_{\rm c}^{\circ} + \lambda_{\rm p}) \tag{5}$$

where

$$f_{\text{theo}} = \mathbf{0.886} |z_{\text{c}}|^{-1} \xi_{\text{M}}^{-1}, \quad \xi_{\text{M}} = \frac{Q}{b} = \frac{e^2}{\epsilon K T b} > |z_{\text{c}}|^{-1}$$
 (6)

 λ_c° is the equivalent conductivity of the counterions in pure solvent, z_c is the valence of the counterion, ξ_M is the charge density parameter, $Q = e^2/\epsilon KT$ is the Bjerrum length (*e* is the electronic charge and ϵ is the dielectric constant of water), *b* is the charge spacing of the polyelectrolyte chain, and λ_p is the equivalent conductivity of the polyions in the solution, given by

$$\lambda_{\rm p} = \frac{279A|z_{\rm c}|^{-1}\ln\kappa r}{1 + 43.2(|z_{\rm c}|\lambda_{\rm c}^{\circ})^{-1}A\ln\kappa r}$$
(7)

where

$$A = \frac{\epsilon KT}{3\pi\eta e} \tag{8}$$

 κ is the Debye–Hückel screening constant

$$\kappa^2 = \left(\frac{4\pi e^2}{\epsilon KT}\right)\frac{c_{\rm p}}{\xi_{\rm M}} \tag{9}$$

and *r* is the radius of the polyions. Equation 6 indicates that f_{theo} only depends on the charge densities and is not a function of the segmental concentration, whereas Λ obtained from eq 5 slightly depends on the concentration because of λ_p . We have used eqs 5–9 to calculate f_{theo} and Λ for the PXT(I) solutions. The results are plotted in Figure 6. The discrepancy between Manning's conductivity theory and the experimental results in the semidilute regime is due to the fact that the former does not consider the overlapping of the polymer chains. The fraction of dissociated counterions should be less than that predicted by eq 6. If we allow the fraction of dissociated counterions in eq 5 to be adjustable, i.e., with *f* to replace f_{theo} in order to fit the experimental data, we found that the predicted



Figure 7. Equivalent conductivities of PXT with various number-averaged molecular weights as a function of square root of segmental concentrations; $M_n = (\blacksquare) 365\ 000$, $(\Box)\ 154\ 000$, $(\bullet)\ 93\ 000$, and $(\bigcirc)\ 25\ 000\ g/mol$.

equivalent conductivities are well matched with the experimental data. The deviation of f from f_{theo} resulted from the overlapping of polyelectrolyte chains influencing the counterion dissociation.

When the molecular weight of PXT was decreased, the fraction of dissociated counterions f was increased as shown in Figure 7. With the increase of f, the repulsion among the intrapolymeric segments is increased, which is believed to cause the increase of conformation index as shown in Figure 3. It should be noted that Mattoussi et al.²² have used the small-angle light scattering technique to measure the radius of gyration (R_G) of PXT in methanol as a function of NaCl concentrations. They found the rapid decrease of R_G with the ionic strength of the medium. The latter is corresponding to the decrease in the dissociation extent of counterions. Similar results were also obtained by our previous study with the chain conformation of PXT estimated by eq 4.²

However, for the PXT(I) with the highest molecular weight, the dissociation extent of counterions is only slightly less than that of the PXT(II), but the conformation index is substantially smaller. It indicated that the increased configurational entropy with the chain length decreased the conformation index of the polymer chains but may not be necessary to decrease the dissociation extent of counterions.

Conclusions

The chain conformations of PXT in salt-free semidilute aqueous solutions were more coiled along with the decrease of counterion dissociation when the molecular weight was increased. However, when the molecular weight was over 150 000 g/mol, the increased configurational entropy affected more on the chain conformations than the dissociation extent of counterions.

Acknowledgment. The authors acknowledge the financial support of the National Science Council in Taiwan, Republic of China, through Grant NSC 88-2216-E002-01.

LA011858K

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