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A Simple Method To Estimate Chain Conformations of Polyelectrolytes in the Semidilute Regime

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ABSTRACT: In semidilute polyelectrolyte solutions, reduced viscosity (η_r) versus concentration (c_p) plots follow the relation $\eta_r \sim c_p{}^n$, where n is dependent on the chain conformations. Using de Gennes' scaling arguments, we show that the average end-to-end distance of a polyelectrolyte chain, $R = N^{\nu}a$ (N is the number of mers in a chain and a is the length per mer), can be estimated by $\nu = (n + 2)/3(n + 1)$. The new scaling relation was employed to estimate the chain conformations of poly(xylylene tetrahydrothiophenium chloride) (PXT) in salt-free and salt-containing aqueous and methanol solutions.

I. Introduction

Polyelectrolytes are charged polymers. In semidilute salt-free systems or solutions with low salt content, polyelectrolyte solutions show an anomalous behavior in that the reduced viscosity η_r abruptly increases with decreasing polyelectrolyte concentration c_p.[1,2] Such a phenomenon is usually described by Fuoss's empirical equation: $\eta_r = A/(1 + Bc_p{}^{-1/2})$, where A and B are constants.[1] Over the past several decades, Fuoss's equation has been often employed to predict the viscometric properties of polyelectrolyte solutions.[3] In addition, de Gennes et al.[4] have derived an expression $\eta_r \sim Nc_p{}^{-1/2}$, where N is the degree of polymerization, by assuming that the polyelectrolyte chains are in a rigid-rod conformation in the semidilute regime. Because of the similarity between two equations, the latter equation has also often been referred to as the “Fuoss law”.

However, the conformation of polyelectrolyte chains is not yet clear. Theoretical efforts to interpret polyelectrolyte expansion in solution have focused on two models, i.e., the chain model and spherical model.[5,6] The first chain model was discussed by Kuhn et al.,[7] who assumed that in dilute solutions the counterions escape from the polyelectrolyte domains so that the polyelectrolyte chains become extended. The chain model has been shown to be oversimplified because a significant fraction of counterions remain in the polymer domains.[6] Recent molecular dynamics (MD) simulations of flexible polyelectrolytes in salt-free solution by Stevens and Kremer[8] do not support the notion of rodlike conformations owing to counterion condensation on the polyelectrolyte chains and chain overlapping in the semidilute regime. The collapse of polyelectrolyte extended chains by counterion condensation has also been theoretically studied by several research groups recently.[9−11] A different approach, the spherical model, was first proposed by Hermans and Overbeek,[12] who assumed that polyelectrolyte chains form a sphere with a uniform charged density in a salt solution. Flory[13] also treated the swelling of polyelectrolytes in the presence of salt as a uniformly charged sphere. However, the spherical model is unrealistic because the polyelectrolyte chains become increasingly asymmetric as they expand. Yethiraj[14] suggested, at his recent theoretical predictions on the structure of polyelectrolyte solutions, that the conformation of polyelectrolyte chains changes from extended to coillike state with increasing the concentration.

Thus, since the conformation of polyelectrolyte chains in the semidilute regime is not clearly defined, the expression $\eta_r \sim Nc_p{}^{-1/2}$ may not be straightforwardly applied. Yamanaka et al.[15] have reported $\eta_r \sim c_p{}^{-0.3}$ for the salt-free sodium poly(styrenesulfonate) (NaPSS) aqueous solutions. To replot the viscometric data of Fuoss and Strauss[1] by double-logarithmic scale, we only obtained $\eta_r \sim c_p{}^{-0.42}$. From the literature survey,[16−18] the exponent of c_p in reality exhibited more or less discrepancies from the Fuoss law depending on the polyelectrolyte solution systems (see Figure 1).

In this study, on the basis of de Gennes' scaling arguments, we derived a simple method to estimate the chain conformations of polyelectrolytes in the semidilute regime with and without containing salt. Then, the obtained scaling relation was employed to estimate the chain conformations of poly(xylylene tetrahydrothiophenium chloride) (PXT), in the salt-free and salt-containing aqueous and methanol solutions. PXT is known as a polymeric precursor of poly(phenylenevinylene) (PPV), which is the first reported polymer possessing the electroluminescent properties.[19] PPV is also a rigid-rod crystalline polymer, which is insoluble and intractable. Thus, PPV thin films were usually prepared by casting the PXT solution and followed by baking to remove the tetrahydrothiophene side groups. Therefore, to study the PPV polymer and its blends, one has to pursue the solution behavior of PXT.[20,21]

II. Revisit to de Gennes' Scaling Arguments[4]

We introduced the concept of flexible polyelectrolyte chains into the de Gennes's scaling arguments[4] by assuming the polyelectrolyte chains to be a succession of segments (or blobs), each of which carries a g-number of monomers in a mesh of the semidilute solution. By referring to the Rouse dynamics and neglecting the

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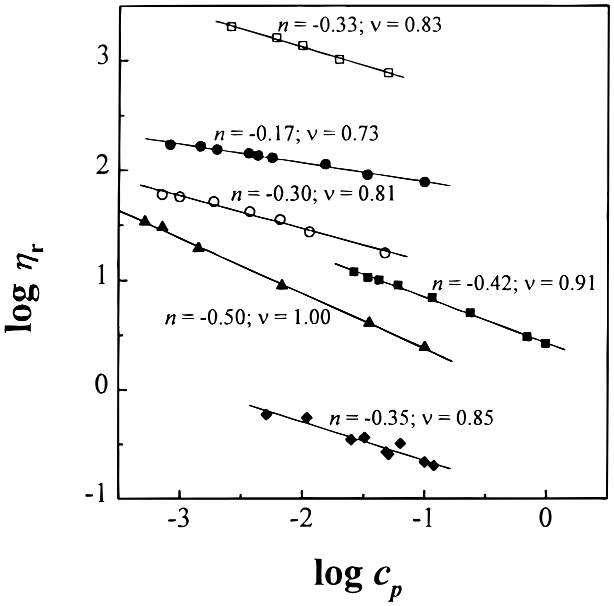

Figure 1. Double-logarithmic plots of η_r versus c_p (in unit of g/dL) of various polyelectrolytes in the semidilute regime of salt-free aqueous solutions: (■) poly(*N*-*n*-butyl-4-vinylpyridonium bromide), $M_w = 2.0 \times 10^5$, data quoted from Fouss and Strauss;[1] (□) sodium hyaluronate, $M_w = 1.5 \times 10^6$, from Roure et al.;[16] (●) NaPSS, $M_w = 6.9 \times 10^5$, from Cohen et al.;[17] (○) NaPSS, $M_w = 1.77 \times 10^5$, from Cohen et al.;[17] (▲) NaPSS, $M_w = 3.1 \times 10^4$, from Cohen et al.;[17] (◆) poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylene-*alt*-1,4-phenylene] sodium salt, $M_w = 1.9 \times 10^4$, from Kim et al.[18] The solid lines with slopes n were obtained by fitting the data with the first least-squares method, whereas ν obtained from eq 6.

entanglement effects, the viscosity of the polyelectrolyte solutions, η, may be expressed as follows[22]

$$\eta - \eta_0 = \frac{1}{36}\rho \bar{r}_0^{\,2} N^* f_0 \qquad (1)$$

where η_0 is the viscosity of solvent, ρ = moles of polymer chains/volume $\sim c_p/N$, $\bar{r}_0^{\,2} = N^*\xi^2$ is the mean-square end-to-end distance of a single chain, ξ is the correlation length or blob size, $N^* = N/g$ is the number of blobs of a single chain, $f_0 = 3\pi\eta_0\xi$ is the friction coefficient of a single blob (here we assume the system is undraining inside the blob) against the solvent, and $g \sim c_p\xi^3$, by assuming that each volume ξ^3 is occupied by one blob on the average. It is noteworthy that the friction coefficient in our case is considered in terms of a single blob instead of a monomer as defined by de Gennes et al.[4] Now we may rewrite eq 1 as follows:

$$\eta_r = \frac{\eta - \eta_0}{\eta_0 c_p} \sim \frac{\pi}{3}\frac{N}{c_p^{\,2}\xi^3} \qquad (2)$$

According to de Gennes et al.,[4] the crossover from dilute to semidilute regime is characterized by a critical concentration $c^* \sim N/R^3$, where R is the average end-to-end distance of polyelectrolyte chains. Because of the overlapping of the 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 solution is governed by the correlation length $\xi(c_p)$ as $c_p \gg c^*$. From the formula of the correlation length suggested by de Gennes et al.,[4]

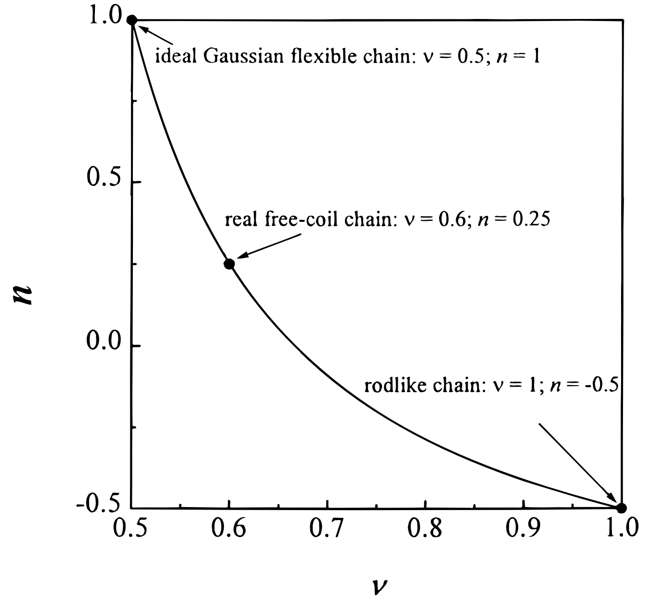

Figure 2. The exponent n in $\eta_r \sim c_p^{\,n}$ versus ν in $R = N^{\nu}a$ as plotted by eq 6.

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

where m is the unknown power of the concentration. For rodlike chains, $R = Na$, where a is the length per mer. Thus, $c^* \sim N/R^3 = N^{-2}a^{-3}$. Both c^* and R depend on N, but ξ does not. So, from eq 3, $m = 0.5$ and $\xi(c_p) \sim c_p^{-0.5}a^{-0.5}$. By inserting eq 2, $\eta_r \sim Nc_p^{-1/2}$, similar to the result obtained by de Gennes's arguments. However, for ideal Gaussian flexible chains, $R = N^{0.5}a$ and $c^* \sim N/R^3 = N^{-0.5}a^{-3}$. From eq 3, we obtain $m = 1$ and $\xi \sim c_p^{-1}a^{-2}$. Again, by inserting eq 2,

$$\eta_r \sim Nc_p \qquad (4)$$

Apparently, different flexibility of the polyelectrolyte chains has different power of concentrion dependence in $\eta_r \sim Nc_p^{\,n}$. Thus, we assume $R = N^{\nu}a$, in which $0.5 \le \nu \le 1$, corresponding to the Gaussian flexible and rigid-rod limiting cases, respectively. From eq 3, $\xi \sim N^{\nu+m-3\nu m}c_p^{-m}$. Since $\xi \sim N^0$, $\nu + m - 3\nu m = 0$. Therefore, $m = \nu(3\nu - 1)^{-1}$. From eq 2, we obtain

$$\eta_r \sim Nc_p^{\,n} \sim Nc_p^{-[(3\nu-2)/(3\nu-1)]} \qquad (5)$$

or

$$\nu = \frac{n+2}{3n+3} \qquad (6)$$

The result is sketched in Figure 2. It can be found that the exponent n changes from $-1/2$ for a rodlike chain conformation to 1 for a Gaussian flexible chain. As for the real free-coil chain ($\nu = 0.6$), $n = 0.25$. Rubinstein et al.[23] 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 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. A similar result was also obtained by Muthukumar,[24] who gave $n = 0.25$ for the polyelectrolyte solutions with high salt content.

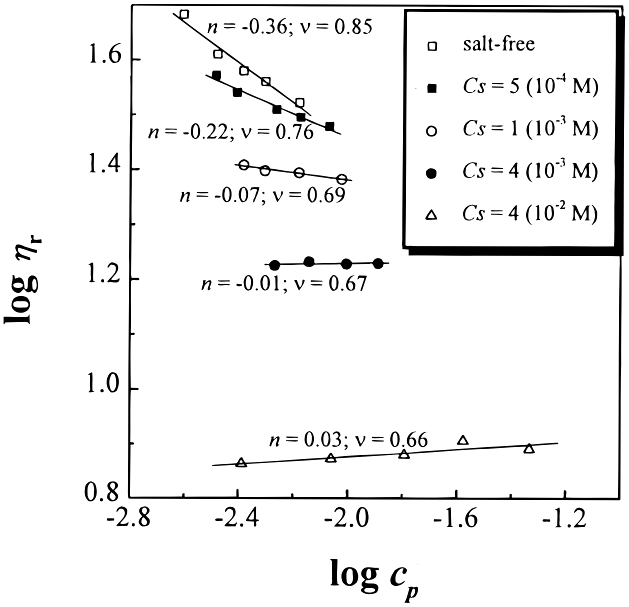

Figure 3. Double-logarithmic plots of η_r versus c_p (in units of g/dL) of PXT aqueous solutions containing various NaCl concentrations. The solid lines with slope n were obtained by fitting the data with the first-order least-squares method, whereas ν obtained from eq 6.

Equation 6 was employed to estimate the chain conformations of the polyelectrolyte solution systems quoted in Figure 1, and the results are also noted in the figure. Among them, the chain conformation of NaPSS in the semidilute regime was found less extended when the chain length was increased. The tendency is agreeable with most of the theoretical predications.[8,25,26] We also found that, in the semidilute regime of salt-free NaPSS solution system, the long and flexible polyelectrolyte chains turned to aggregate with each other.[27] A similar scaling method was also employed by Witten and Pincus[28] to explain how the persistence length of a charged polymer is influenced by other polymers. In the following, the obtained scaling relation was employed to estimate the chain conformations of PXT in aqueous and methanol solutions with and without containing salt.

III. Experimental Section

The PXT polyelectrolyte with a number-average molecular weight of 365 000 and a dispersity of 3.2 was prepared via a sulfonium precursor route,[21] the detailed description of which has been reported elsewhere.[29] To overcome the inherent problems in determining the molecular weight of polyelectrolyte, we have replaced the ionic moieties with neutral thiophenolate groups by following ref 30. The molecular weight was then measured by gel permeation chromatography (Testhigh series III pump and model 500 UV detector with THF as a mobile phase). Water used to prepare the aqueous solution was purified by the Barnstead Easypure RF system to a resistivity of 18.3 MΩ·cm, and the methanol for the methanol solution was HPLC grade. The polymer solutions were then prepared by volumetric dilutions for concentrations ranging from 0.015 to 0.001 g/dL. Polymer solutions with added sodium chloride (NaCl) salts were prepared from the highest polymer concentration first and then gradually diluted with sodium hydroxide aqueous (or methanol) solutions having predetermined concentrations. All viscosity measurements were carried out at a constant temperature of 25 ± 0.01 °C using a capillary Ubbelohde viscometer (type 0A, Cannon Co.) immersed in a thermostatic water bath (TAMSON co., model TV 2000). 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.

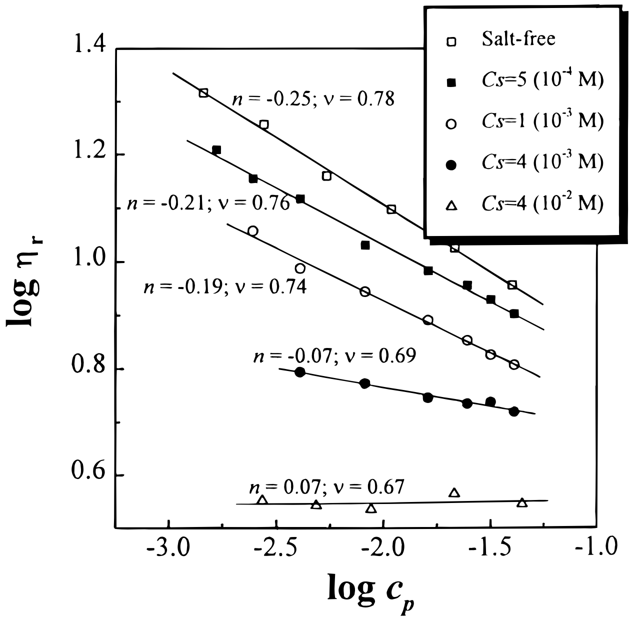

Figure 4. Double-logarithmic plots of η_r versus c_p (in units of g/dL) of PXT methanol solutions containing various NaCl concentrations. The solid lines with slope n were obtained by fitting the data with the first-order least-squares method, whereas ν was obtained from eq 6.

IV. Results and Discussion

Figures 3 and 4 show the double-logarithmic plots of reduced viscosity η_r versus the concentration c_p of PXT in salt-free and NaCl-salt containing aqueous and methanol solutions. For the salt-free aqueous solution, the measured n is -0.36 and the calculated ν by eq 6 is 0.85. Thus, the number-average end-to-end distance R of PXT chains in the semidilute regime is 3406 Å, about one-third of the fully extended chain length (Na = 10 310 Å). On the other hand, for the salt-free methanol solution, n is -0.25, so $\nu = 0.78$ and R = 2031 Å, about one-fifth of the fully extended length.

According to the molecular dynamics study on the flexible polyelectrolytes in solutions,[8] the counterion's condensation on the polyelectrolyte chains and chain overlapping in the semidilute regime are responsible for the shrinkage of chains. From the Manning's limiting law,[31] uncondensed fraction of the counterions, f, can be estimated by

$$f = \frac{0.886\epsilon kTa}{e^2} \tag{7}$$

where e is the protonic charge, ϵ the dielectric constant of solvent, k Boltzmann's constant, and T the absolute temperature. For the salt-free PXT aqueous and methanol solutions, $f = 0.76$ and 0.32, respectively, at 25 °C. Therefore, it is possible that more condensed counterions in the salt-free methanol solution shrank the polyion chains more in comparison with the aqueous solution, because the electrostatic repulsion from the adjacent segmental charges would be weaker to counterbalance the entropy effect. Theoretical predictions on the shrinkage of the chains with increasing counterion condensation have been reported recently by Schiessel and

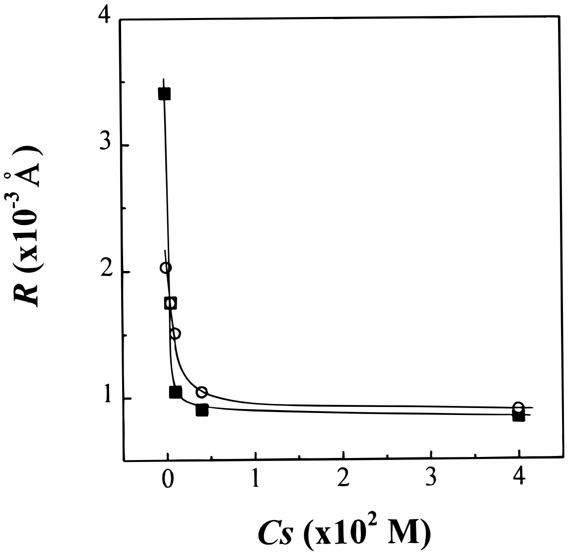

Figure 5. Average end-to-end distance R of PXT as a function of C_s in (■) aqueous and (○) methanol solutions.

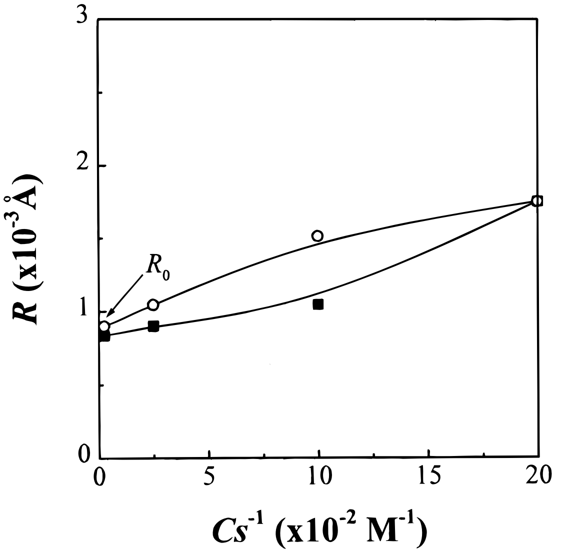

Figure 6. Plot of R versus C_s^{-1} of PXT in (■) aqueous and (○) methanol solutions.

Pincus.[10] They and other independent research group[11] also predicted the occurrence of a first-order-type phase transition of chain collapse when nearly all counterions are condensed. However, although the Manning's limiting law has proven very successful in the experimentally accessible dilute ragime,[31] it may underestimate the number of condensed counterions in the semidilute regime as suggested by Kuhn et al.[32]

On the other hand, as for the chain overlapping in the semidilute regime, researchers often reported that the polyelectolyte chains turn to aggregate to form a multichain cluster in the salt-free aqueous solution as observed by dynamic light scattering experiments.[33-37] We have also investigated the chain aggregation phenomenon of NaPSS in the salt-free aqueous solution by dialysis.[23] According to Stevens and Kremer,[8] when the concentration of polyelectrolyte solution is increased, the monomer−monomer repulsion is more strongly screened by forcing the counterion clouds closer to the monomers. As a result, the chains should contract by overlapping. However, Levin et al.[38] suggested that the attraction between like charged polyions inside a polyelectrolyte solution is short-ranged and exists only in the presence of multivalent counterions.

For salt-containing cases, obviously, the viscosity decreased with the NaCl concentration C_s so that the exponent n decreased with adding salts for both aqueous and methanol solutions. By using eq 6 to calculate ν in $R = N^{\nu}a$, the resulting average end-to-end distance of polyelectrolyte chains as a function of salt concentrations in aqueous and methanol solutions is plotted in Figure 5. The trend of changes in methanol solutions is similar to that of the reported radii of gyration measured by light scattering techniques on the same PXT solution systems.[20] By following a similar approach to plot the R vs C_s^{-1} as shown in Figure 6, the asymptotic value of the average end-to-end distance of neutral (uncharged) chains at a limit of $C_s^{-1} \rightarrow 0$, R_0 is 830 Å for aqueous solution and 900 Å for methanol solution. The slightly larger size of neutral chains in the methanol solution compared to the aqueous solution indicates that the methanol is a better solvent for neutral PXT chains than water.

V. Conclusions

In this contribution, we provided a simple and useful method to estimate the chain conformations of polyelectrolytes in the semidilute regime, by using the double-logarithmic plots of the reduced viscosity versus segmental concentrations. The obtained scaling relation is able to estimate the average end-to-end distance of polyelectrolyte chains in the salt-free and salt-containing solution systems as long as their chain length is over the entanglement limit.

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