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Cooperative Diffusion of Semidilute Polyelectrolyte Solutions: Analysis by Renormalization Group Theory

Lixiao Wang and Victor A. Bloomfield*

Department of Biochemistry, University of Minnesota, St. Paul, Minnesota 55108.

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ABSTRACT: The renormalization group theory of Oono et al. for the concentration dependence of the cooperative diffusion of neutral polymer in semidilute solutions is applied to the polyelectrolyte sodium poly(styrenesulfonate) (NaPSS) in aqueous salt solution. This theory predicts that the reduced diffusion coefficient $D_c(C)/D_c(0)$ is a universal function of the reduced concentration A_2C, where A_2 is the thermodynamic second virial coefficient. It satisfactorily explains the experimental results of Koene et al. and Wang et al. over a range of salt concentrations from 0.01 to 0.15 M in semidilute solution. The low salt behavior of NaPSS is that expected in a good solvent, while that observed at higher salts shows a trend toward Θ solvent behavior. In dilute NaPSS solutions with low salt, the diffusion coefficient is overestimated compared to renormalization group theory predictions, perhaps due to chain expansion beyond the neutral good solvent limit. A plot of $D_c(C)/D_c(0)$ versus KC, where K is the diffusion virial coefficient, gives universal behavior characteristic of the good solvent limit over the entire concentration range, independent of polymer molecular weight or salt concentration. However, experimental uncertainties in K limit the reliability that may be ascribed to this result.

Introduction

This short report applies the renormalization group theory by Oono et al.[1,2] to the concentration dependence of the cooperative diffusion of semidilute polyelectrolyte solutions over a 15-fold range of salt concentrations. It shows that cooperative diffusion in semidilute polyelectrolyte solutions can be explained not only by scaling theory but also by the renormalization group theory.

The renormalization group theoretical approach has been successful in describing static properties of dilute[3,4] and semidilute[5,6] neutral polymer solutions. Transport properties of dilute solutions have also been studied[7] with the aid of the renormalization group theory. Wiltzius et al.[8] studied static and dynamic properties of polystyrenes in good and marginal solvents and found that the product of molecular weight (M) and osmotic compressibility (the derivative of the osmotic pressure (π) with respect to concentration (C), $M(\partial\pi/\partial C)T$, is a universal function of scaled concentration, independent of solvent quality and molecular weight. They also found that the ratio of dynamic length (ξ_H) to hydrodynamic radius (R_H) is a function only of the reduced concentration, KC, where K is determined from a virial expansion of the diffusion coefficient. Very recently, the cooperative diffusion constant in good solvents has been studied with the aid of the renormalization group methods based on the conventional minimal model—that model which takes into account the chain connectivity, the excluded volume interaction, and the hydrodynamic interaction (or the fluctuation of the solvent velocity field) by Oono et al.[1,2] The results agree well with the experimental results of Wiltzius et al.[8] Burchard[25] has described the static and dynamic properties of linear and star polystyrene and other polymers in terms of the renormalization group theory.

The situation with regard to polyelectrolytes is much less well developed, owing to complications arising from long-ranged polyion–polyion and polyion–small ion electrostatic interactions. Despite these difficulties, interest in polyelectrolyte dynamics has been considerable,[9,10] and certain aspects of the scaling theories of polyelectrolyte solutions have been established.[11-14] Several dynamic light scattering studies of polyelectrolytes have already been reported in the literature.[9,10,16-22] Many have reported the observation of a fast cooperative diffusion coefficient, D_c(fast), and a slow diffusion coefficient, D_c(slow), under low salt conditions.[9,10] Koene et al.[16] and Grüner et al.[19] reported on the polyelectrolyte concentration dependence of cooperative diffusion coefficients, which agrees reasonably well with the theoretical predictions of scaling theory. Wang et al. studied polyelectrolyte and salt concentration

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dependences of self-diffusion and cooperative diffusion coefficients in semidilute solutions of sodium poly(styrenesulfonate),[20-22] which were explained in the context of scaling relations developed by de Gennes et al.,[11] Odijk,[12] and Skolnick and Fixman.[14]

In this paper, we show that the polymer and salt concentration dependences of cooperative diffusion coefficients of polyelectrolytes can also be explained by the renormalization group theory. The scaling theory cannot derive the prefactors in the scaling relations. The renormalization group theory can describe the whole region from dilute to semidilute behavior with a prediction of the prefactors.

Results and Discussion

Theoretical Background. The renormalization group theoretical results for the concentration dependence of the cooperative diffusion constant were derived by Oono et al.[1,2] in detail and will be described only briefly here. The cooperative diffusion coefficient, D_c, appears in the hydrodynamic description of the fluctuation of the monomer density field, ρ, as[23]

$$\partial\rho/\partial t = D_c\nabla^2\rho \qquad (1)$$

The cooperative diffusion coefficient can be written as

$$D_c(C) = s(1/N)(\partial\pi/\partial C)_T \qquad (2)$$

where π is the osmotic pressure, C the polymer concentration, N the degree of polymerization, and s the sedimentation coefficient defined by

$$v = sf_m \qquad (3)$$

with v being the velocity of the center of mass of a polymer and f_m the external force (e.g., gravity) per monomer.

Oono et al.[1,2] combined the expression for osmotic compressibility, $(\partial\pi/\partial C)_T$, calculated by Ohta and Oono[24] with a generalized Kirkwood–Riseman formalism for the sedimentation coefficient to obtain the following results for the monodisperse polymer system:

$$D_c(C)/D_c(0) = (1 + X)^{-(3\epsilon/8)[Z/(1+Z)]\{1/[1-(1+Z)^{-3/4}]\}}[1 + [[1 + (\epsilon/8)(Z/(1 + Z))]X + (\epsilon/4)(Z/(1 + Z))[(\ln (1 + X))/X - 1]] \times \exp\{(\epsilon/4)(Z/(1 + Z))[1/X - [1/X^2 - 1] \ln (1 + X)]\}] \qquad (4)$$

X is a reduced concentration, related to the second virial coefficient, A_2, by

$$X = 16[(1 + Z)/(8 + 9Z)]A_2C \qquad (5)$$

Z is an interaction parameter which describes the crossover between Gaussian ($Z = 0$) and self-avoiding or good solvent ($Z = \infty$) limits. The order of the expansion leading to eq 4 is $\epsilon = 4 - d$, where d is the spatial dimensionality.

Wiltzius et al.[8] introduced a more convenient plot of the reduced dynamic length, ξ/R_H, versus a suitably scaled concentration, KC, where the dynamic length scale, $\xi(C)$, is given by

$$D_c(C) = kT/6\pi\eta_0\xi(C) \qquad (6)$$

and K is the diffusion virial coefficient defined as

$$D_c(C)/D_c(0) = 1 + KC + O(C^2) \qquad (7)$$

Theoretically, KC can be obtained by expansion of eq 4 with X from eq 5:

$$KC = [\exp\{(\epsilon/8)(Z/(1 + Z))\} - (3\epsilon/8)(Z/(1 + Z)) \times [1 - (1 + Z)^{-3/4}]^{-1}]16[(1 + Z)/(8 + 9Z)]A_2C \qquad (8)$$

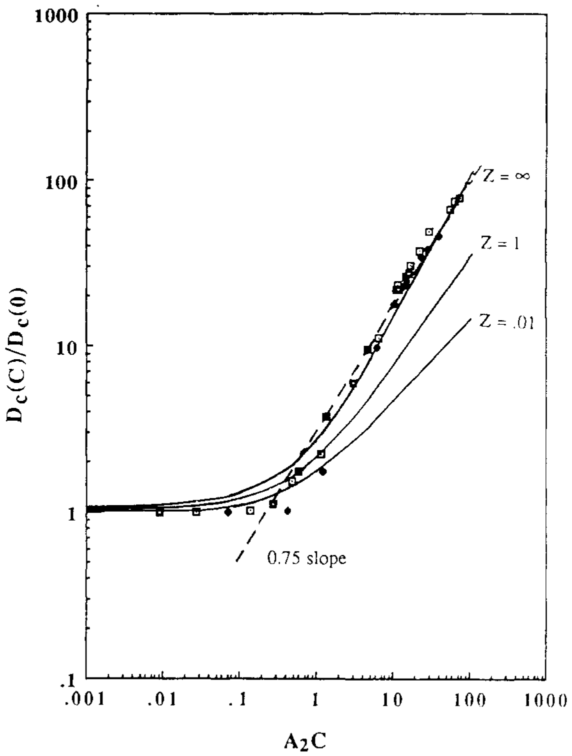

Figure 1. Reduced cooperative diffusion coefficient $D_c(C)/D_c(0)$ as a function of the reduced concentration A_2C (A_2 being the second virial coefficient) for various molecular weight NaPSS in 0.01 M NaCl. Experimental diffusion coefficients are taken from Koene et al.[16] and A_2 values from Takahashi et al.[15] Molecular weights of sodium poly(styrenesulfonate) are 1.2 × 10^6 (◘), 6.5 × 10^5 (◆), and 4.0 × 10^5 (■). The dashed line has a slope of 0.75 predicted from scaling theory. The three curves are calculated from renormalization group theory, eq 4 and 5. The numbers beside the curves denote the value of the crossover parameter Z. $Z = \infty$ is the self-avoiding limit (good solvent limit) and $Z = 0$ is the Θ limit. In the semidilute region, the data follow the curve for $Z = \infty$.

Analysis of Experimental Data. The analysis is applied to data[16,22] on sodium poly(styrenesulfonate) (NaPSS) with molecular weights ranging from 177 000 to 1 200 000 in salt concentrations from 0.01 to 0.15 M. The samples were characterized by the manufacturer as having $M_w/M_n = 1.1$ and a degree of sulfonation close to unity. The cooperative diffusion coefficients, measured by dynamic light scattering, were obtained from the tabulations of Koene et al.[16] and Wang et al.[22] The diffusion virial coefficients, K, were determined by fitting $D_c(C)/D_c(0)$ to a quadratic in C, as in eq 7, and taking the linear term. The thermodynamic second virial coefficients, A_2, were obtained from the tabulation of Takahashi et al.,[15] who determined them by elastic light scattering with samples obtained from temperature reduction fractionation. If A_2 values at certain salt concentrations were not available, they were obtained by interpolation.

Plots of log $[D_c(C)/D_c(0)]$ versus log (A_2C) in 0.01 M NaCl for three different molecular weights are shown in Figure 1. This figure shows that $D_c(C)/D_c(0)$ is a function of A_2C, independent of molecular weight over the entire range of polymer concentration. Apparently, scaling both $D_c(C)$ and C in terms of the measured quantities $D_c(0)$ and A_2 removes sample dependence sufficiently to make this clear. The dashed line in the figure has a slope of 0.75 as predicted from Odijk's scaling theory for polyelectrolytes with added salt.[12] The experimental data are in reasonable agreement with this prediction. This scaling treatment was originally used by Koene et al.[16] and Wang et al.[22] The same experimental data are compared with the calculated

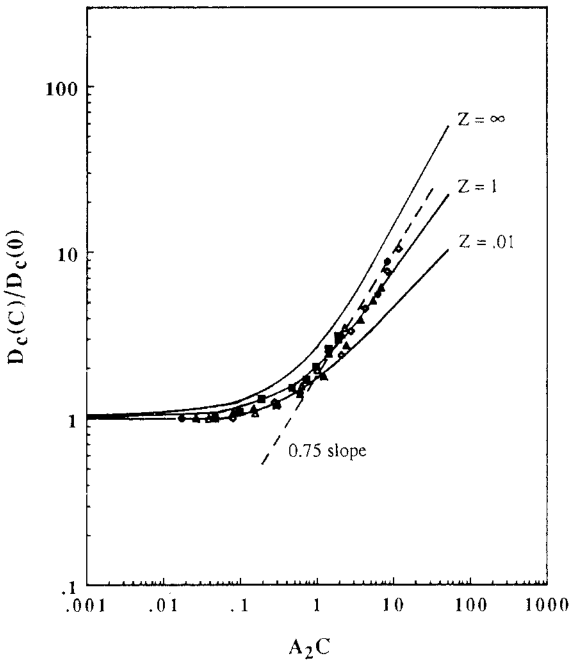

Figure 2. Reduced cooperative diffusion coefficient $D_c(C)/D_c(0)$ as a function of the reduced concentration A_2C for various molecular weight NaPSS in 0.10 and 0.15 M NaCl. Experimental diffusion coefficients are taken from Koene et al.[16] and Wang et al.[22] and A_2 values from Takahashi et al.[15] Molecular weights of sodium poly(styrenesulfonate) and NaCl concentrations are 6.5 × 10^5, 0.10 M (◇); 6.5 × 10^5, 0.15 M (▲); 2.15 × 10^5, 0.15 M (■); and 1.77 × 10^5, 0.15 M (△). The calculated curves have the same meaning as in Figure 1.

values for a good solvent ($Z = \infty$) of the renormalization group theory of Oono et al.[1,2] in Figure 1. Agreement in the semidilute polyelectrolyte solutions is remarkable, in view of the fact that there are no adjustable parameters and no vertical rescaling of any kind. Thus, the chain conformation of sodium poly(styrenesulfonate) in 0.01 M NaCl reaches the good solvent limit ($Z = \infty$) in semidilute polyelectrolyte solutions. At low polymer concentrations, the scaled diffusion coefficient changes only very slightly with A_2C, in qualitative agreement with theoretical predictions.

Similar results for 0.10–0.15 M NaCl solutions are shown in Figure 2. $D_c(C)/D_c(0)$ is a molecular weight independent function of A_2C over the entire concentration range. In the semidilute regime, the data are in reasonable accord with the 0.75 slope predicted by the scaling theory. The data fit reasonably well the curve for $Z = 1$ computed from renormalization group theory.[1,2] Thus, the chain conformation of sodium poly(styrenesulfonate) moves from the good solvent limit ($Z = \infty$) toward the Θ limit ($Z = 0$) in semidilute solutions as the salt concentration is increased. This change is consistent with the expected variation of solvent quality with salt concentration, since 3.1 M KCl and 4.17 M NaCl have been established as Θ solvents for NaPSS by Takahashi et al.[15] This variation is intuitively expected in dilute solutions, since low salt causes a highly expanded chain owing to electrostatic repulsions, and increasing salt screens these repulsions, leading to more compact chain conformation. However, it is not so obvious that this could have been observed in semidilute solutions, where the polyion itself should contribute significant screening even at low salt.

This transition from good to less good solvent with increasing salt in the semidilute regime is shown in more detail in Figure 3, which combines the low salt and high salt data from Figures 1 and 2 with intermediate salt concentration data at 0.025 and 0.05 M.

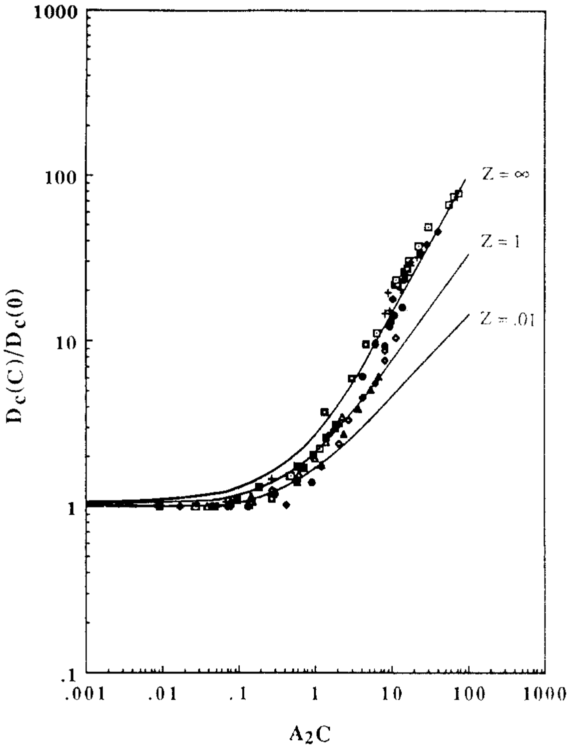

Figure 3. Reduced cooperative diffusion coefficient $D_c(C)/D_c(0)$ as a function of the reduced concentration A_2C for various molecular weight NaPSS at salt concentrations from 0.01 to 0.15 M. Experimental diffusion coefficients are taken from Koene et al.[16] and Wang et al.[22] and A_2 values from Takahashi et al.[15] Molecular weights of sodium poly(styrenesulfonate) and NaCl concentrations are 1.2 × 10^6, 0.01 M (⊡); 4.0 × 10^5, 0.01 M (◘); 6.5 × 10^5, 0.01 M (◆); 6.5 × 10^5, 0.025 M (+); 6.5 × 10^5, 0.05 M (●); 6.5 × 10^5, 0.10 M (◇); 6.5 × 10^5, 0.15 M (▲); 2.15 × 10^5, 0.15 M (■); 1.77 × 10^5, 0.15 M (△). The calculated curves have the same meaning as in Figure 1.

Although agreement between experimental data and predictions of renormalization group theory is remarkably good in semidilute polyelectrolyte solutions, the theory does not work so well in dilute solution. $D_c(C)/D_c(0)$ is consistently overestimated, especially in the low salt, good solvent conditions shown in Figure 1. This behavior was not observed with neutral polymer solutions for which the theory was developed, such as polystyrene in toluene.[1,2,8] One possible resolution to this conflict is that NaPSS is expanded well beyond the good solvent limit in 0.01 M NaCl. The molecular weight exponent of the Mark–Houwink–Sakurada relation has been shown to be 0.89 for 0.01 M NaCl,[15] while 0.75 is expected for a good solvent and an uncharged polymer. When the polymer concentration is reduced in low salt, the chain expands to become stiffer, leading to a smaller than predicted translational diffusion coefficient. It must be recognized, of course, that this idea is extraneous to the well-defined concepts of renormalization group theory.

Furthermore, there still is a solvent quality effect on the reduced cooperative diffusion coefficient even in semidilute polyelectrolyte solutions, as shown in Figure 3. That is, $D_c(C)/D_c(0)$ is not simply a universal function of A_2C but also depends on Z. A similar effect was also observed by Wiltzius et al.[8] for neutral polystyrene solutions. They found that the quantity ξ/R_G, which reflects static properties, depends only on A_2C both experimentally and theoretically and can be explained in terms of static properties such as $(\partial\pi/\partial C)_T$. However, one might not expect a dynamic quantity, $\xi/R_H = D_c(0)/D_c(C)$, to depend only on A_2C. This was attributed[8] to the sensitivity of R_H

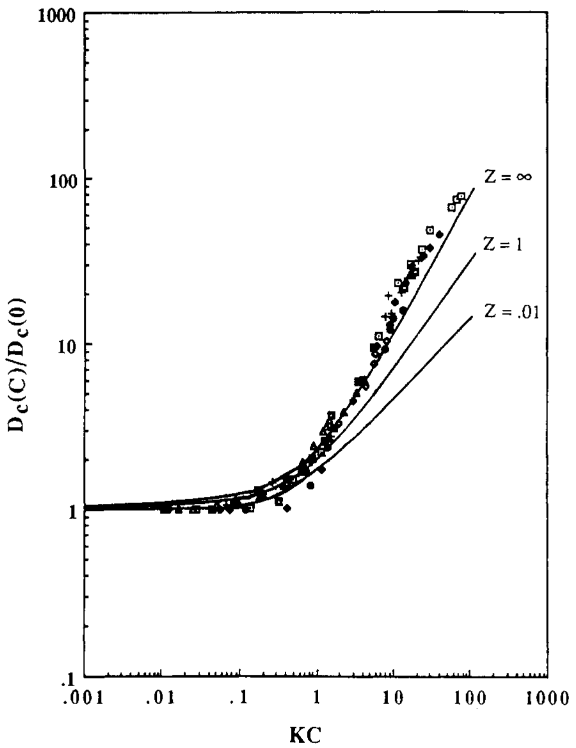

Figure 4. Reduced cooperative diffusion coefficient $D_c(C)/D_c(0)$ as a function of the reduced concentration KC, where K is the diffusion virial coefficient, for various molecular weight NaPSS at salt concentrations from 0.01 to 0.15 M. K was obtained from a quadratic fit of D_c versus C, from the data of Koene et al.[16] and Wang et al.[22] Molecular weights of sodium poly(styrenesulfonate) and NaCl concentrations of the symbols are the same as in Figure 3. The calculated curves have the same meaning as in Figure 1.

to polymer statistics at short distances. It is possible that even at $C = 0$ much larger values of M_w would be required for R_H to become asymptotic than are necessary for R_G.[8] The spread of experimental data in Figure 3 may be due to the different ratio of R_H/R_G at the different salt concentrations.[20] Wiltzius et al.[8] suggested that a $D_c(C)/D_c(0)$ versus KC plot would be a universal curve essentially independent of both molecular weight and solvent quality for neutral polymer solutions.

We have tried the same approach with sodium poly(styrenesulfonate), with the results shown in Figure 4. Unfortunately, some of the experimental data are not precise enough to determine K within better than 50%. It is well established that D_c is only a weak function of C, because of approximate cancellation of hydrodynamic and thermodynamic virials, and this leads to large errors in the determination of K. This may account for the rise of the points above even the $Z = \infty$ line at higher concentrations. Therefore, we have explored ways to determine K theoretically. One way is through eq 8, since A_2 is known for these systems and Z can be estimated, as shown above. Another is through the equation

$$K = 2A_2 - \phi - k_s \qquad (9)$$

where ϕ is the polymer volume fraction, essentially zero in dilute solution, and k_s is the frictional virial coefficient. Two leading theories for k_s are those of Yamakawa[26] for the random-flight model ($k_s = 1.2A_2 + 4\pi N_A R_H^3/3M$) and Pyun and Fixman[27] for hard spheres ($k_s = 7.16 \times (4\pi N_A R_H^3/3M)$).

Table I compares the experimental values of K with these theoretical ones. K decreases with an increase of the salt concentration, consistent with the anticipated effects of solvent quality and chain expansion. Except for the 0.15 M salt systems, where K is smallest and therefore hardest to measure accurately, the Pyun–Fixman and Yamakawa theories consistently bracket the data: the former on the high side, the latter on the low. Figure 5 shows that, when K is calculated according to the Pyun–Fixman theory, the points fall adequately within the limits of renormalization group theory predictions and generally best follow the $Z = \infty$ curve. The Yamakawa theory (not shown) gives worse agreement than renormalization group theory expectations. In low salt solutions, the Pyun–Fixman values agree remarkably well with the K values calculated from eq 8 with $Z = \infty$. In high salt, agreement is best with the values calculated with $Z = 0.01$. This trend is consistent with the anticipated change of chain conformation from good solvent to Θ solvent behavior as the salt concentration is

Table I
Diffusion Virial Coefficients

M_w	C_s, M	K_{exp}[a]	K_{calc}[b]	K_{calc}[c]	K_{calc}[d]	K_{calc}[e]
400K	0.01	1091	1237	920	1213	647
650K	0.01	1500	2011	1496	2232	1089
1200K	0.01	2802	3712	2761	3231	1885
650K	0.025	710	977	727	999	517
650K	0.05	440	633	471	567	324
650K	0.10	244	461	343	405	235
650K	0.15	167	381	284	272	185
215K	0.15	88	127	94	81	60
177K	0.15	51	104	77	65	49

[a] The values were reduced from experimental data, some of them have errors ~±50%. [b] The values were calculated from eq 8 with $Z = \infty$. [c] The values were calculated from eq 8 with $Z = 0.01$. [d] The values were calculated from $K = 2A_2 - \phi - k_s$, where ϕ is the polymer volume fraction, essentially zero in dilute solution, and $k_s = 7.16(4\pi N_A R_H^3/3M)$ by Pyun and Fixman[27] for hard spheres. R_H were calculated from D_0 in dilute solution. [e] The values were calculated from $K = 2A_2 - \phi - k_s$ with $k_s = 1.2A_2 + (4\pi N_A R_H^3/3M)$ by Yamakawa[26] for random-flight model.

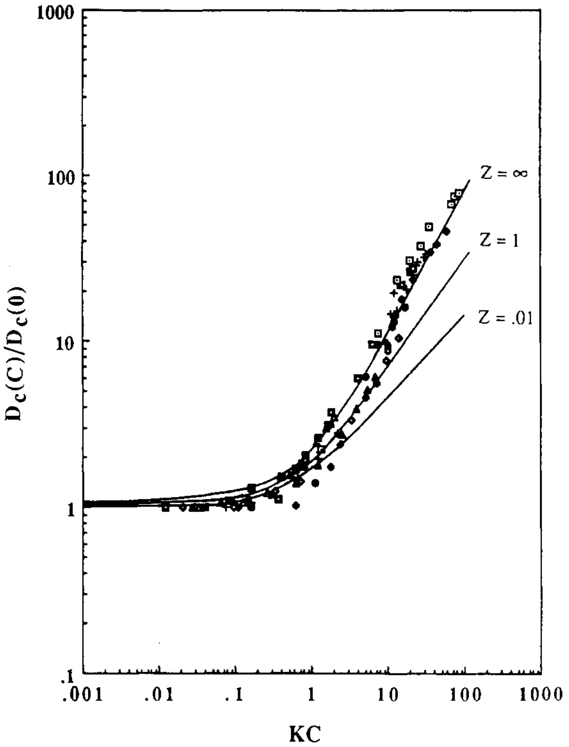

Figure 5. Reduced cooperative diffusion coefficient $D_c(C)/D_c(0)$ as a function of the reduced concentration KC for various molecular weight NaPSS at salt concentrations from 0.01 to 0.15 M. The K values were calculated from the theory by Pyun and Fixman,[27] as detailed in Table I. Molecular weights of sodium poly(styrenesulfonate) and NaCl concentrations of the symbols are the same as in Figure 3. The calculated curves have the same meaning as in Figure 1.

increased.

Conclusions

In the presence of added salt in the 0.01-0.15 M NaCl range, the dynamics of the polyelectrolyte sodium poly(styrenesulfonate) in dilute and semidilute solution are very similar to those of neutral polystyrene. The polyion concentration dependence of the cooperative diffusion coefficient in semidilute solutions is consistent with the predictions of both scaling and renormalization group theories. The dynamic quantity $D_c(C)/D_c(0)$ is a function only of A_2C for a given solvent quality parameterized by the interaction parameter (Z) but shifts to a curve characteristic of lower Z as salt increases and the solvent approaches a Θ solvent. In contrast, $D_c(C)/D_c(0)$ appears to be a universal function of KC, independent of molecular weight or salt concentration, following the curve predicted for $Z = \infty$. However, experimental uncertainties in K demand that this conclusion be regarded as preliminary.

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Registry No. NaPSS, 62744-35-8.

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Influence of Chemical Disorder on the Statistics of a Semiflexible Chain

Glenn H. Fredrickson

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received October 10, 1988; Revised Manuscript Received December 13, 1988*

ABSTRACT: The effects of quenched chemical disorder on the statistical properties of a semiflexible chain are investigated. A simple model with Gaussian fluctuations in the local persistence length is introduced, and its properties are studied to first order in the variance of the disorder. The polymer is found to be expanded relative to a (homopolymer) chain with the average persistence length. The model and results should be relevant to the phase behavior and characteristic dimensions of random copolymers with main-chain mesogens, such as those investigated by Stupp et al. [*Macromolecules* **1988**, *21*, 1217-1234].

1. Introduction

Stupp and colleagues have recently reported[1-3] the synthesis, characterization, and thermotropic phase behavior of a series of copolymers that contain two rigid (mesogenic) monomers (denoted A and B) and a flexible (spacer) monomer (denoted C). One copolymer possessed an ordered sequence of structural units (repeat unit CABCBA), while a second was a random copolymer with the same average composition, but the sequence of A, B, and C being statistically disordered. Among the interesting findings reported in ref 1-3 is the observation that the ordered copolymer exhibits a sharp nematic to isotropic transition over a narrow range of temperatures, while the chemically disordered copolymer shows a broad biphasic region separating the phases of different symmetry. Stupp et al.[3] interpreted this finding by modeling the disordered chains as thermotropic homopolymers, but with a distribution of persistence lengths ("polyflexibility"). By incorporating this distribution into an existing theory for the nematic to isotropic transition in main-chain homopolymers, they were able to reproduce various features of the experiments.

While the influence of chemical disorder on polymeric phase transitions is certainly a fascinating subject, the