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Novel Dynamic Scaling Hypothesis for Semidilute and Concentrated Solutions of Polymers and Polyelectrolytes

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ABSTRACT: We introduce a dynamic scaling hypothesis which connects the self-diffusion of a chain with the viscosity of the macromolecular solution. It applies to both semidilute and concentrated solutions and leaves the detailed motion of the chains unspecified. When it is valid, one is able to measure the density ν of effective dynamic units in the transient network of entangled chains. The feasibility of the hypothesis is shown for aqueous poly(ethylene oxide) and sodium poly(styrenesulfonate), polymers not at all conforming to the usual scaling dynamics. Surprisingly, the density ν is not very sensitive to charge or the addition of salt.

Introduction

A concrete mechanism for the motion of individual chains is invoked in the usual scaling dynamics of polymers.[1] For complex macromolecular fluids like polyelectrolytes, a formulation of the chain dynamics is hampered by a poor understanding of chain entanglement, the concentration dependence of the polyion conformations, and the effect of electrohydrodynamic dissipation arising from the strong coupling of the polyions to the small ions. Moreover, it is well-known that many polymers do not obey mechanistic scaling dynamics.[1] That being the case, we wish to introduce a simple scaling hypothesis which does not rely on a precise mechanism for the macromolecular motion and applies to semidilute polymer solutions, whether or not they are charged. It is not necessary for the chain dynamics to conform to reptation,[1] Rouse,[2] or other models proposed in the literature.

We argue that there should be a general connection between the self-diffusion of a chain and the viscosity within a wide range of concentrations. The fact that there might be some kind of connection is of course not a new proposal as such. For simple liquids, Zwanzig presented a simple motivation for a variant of the Stokes–Einstein formula.[3] For polymers, Graessley and others pointed out the importance of the relation between the two variables.[4] Nevertheless, these authors[3,4] employed microscopic mechanisms. Our scaling hypothesis is derived by eliminating a time scale associated with the global dynamics of a chain. It is not necessary to know how the chain moves. It turns out that the hypothesis can be checked empirically via the dependence of a certain quasi-static scaling variable on the molar mass.

We will test the scaling hypothesis on two different polymeric systems. The first is poly(ethylene oxide) (PEO) in water which is a model system for a neutral polymer in a good solvent. The second is a strong linear polyelectrolyte, sodium poly(styrenesulfonate) (NaPSS), in water. Our main emphasis is on salt-free solutions, but in several preliminary experiments the solvent quality is varied by adding salt.

In the following section we introduce our dynamic scaling hypothesis. A brief description of experimental methods will then be given. Next, we discuss the results on PEO in water. We need additional hypotheses to analyze the salt-free solutions of NaPSS. Finally, several tentative conclusions are drawn for the NaPSS solutions with added salt.

Scaling Hypothesis

The macromolecular solution is semidilute or concentrated: the chains interpenetrate so the excluded volume effect, whatever its origin, is screened in a *static* sense at least. For long linear chains the mean square extension ($\equiv R^2$) is then proportional to the contour length or polymer mass. Suppose we are able to ascertain the self-diffusion coefficient D_s of a single chain unambiguously (this could be the case in a pulsed field gradient NMR experiment, at least under certain conditions). The relation

$$D_s \equiv R^2/\tau \qquad (1)$$

defines a time scale τ in which a test chain diffuses out of its original domain of size R^3. Hence we are assuming there are no other relevant scales (static or dynamic) larger than R. We need not specify the detailed dynamics of the surrounding fluctuating network of other chains, nor whether the probe diffuses in or out of an effective tube, nor any other mechanism. Very strong fluctuations in the chain configuration would render eq 1 meaningless, but then the nondiffusional signature of the chain motion would show up in the experiment (the mean square displacement of a chain would no longer be proportional to time). A general theory for τ is very involved but we now argue that τ may be eliminated via the viscosity.

After a time of order τ, there is virtually nothing left of the original network existing at time $t = 0$. The probability of two test chains initially occupying essentially the same domain of size R^3 and overlapping somewhat at a later time t, decays rapidly to zero for $t > O(\tau)$. If the polymer solution is sheared at $t = 0$, it flows after a duration $t = O(\tau)$ because a test chain has lost almost all memory of its original position and configuration at $t = 0$. Clearly, then, τ represents an approximate upper bound for the time it takes a chain to disentangle, i.e. escape from its original confining environment. At this stage, we introduce our scaling postulate: we hypothesize that the solution does not flow even at times earlier than $O(\tau)$; τ also signifies a

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disentanglement time. In other words, we propose there is only one relevant time scale pertaining to these two types of chain motion. The breaking apart of the transient network under shear is directly related to the self-diffusion of the individual chains although we do not appeal to any specific mechanism for the dynamics. Our hypothesis allows us to generalize a scaling relation introduced previously by de Gennes[1] for polymer melts:

$$\Delta\eta \simeq E\tau \tag{2}$$

This is derived by analyzing the transition of the polymer network under constant shear, from an elastic rubber to a flowing Newtonian liquid, the crossover occurring after a time of order τ. The increment $\Delta\eta$ occurs in eq 2 since the dissipation associated with the motion of the polymer chains is proportional to $\Delta\eta \equiv \eta - \eta_0$ where η is the viscosity of the solution and η_0 that of the solvent. When the chains are entangled dynamically, the elastic modulus E has to be interpreted in terms of a temporary elastic network presumed to exist for times shorter than $O(\tau)$. Otherwise, whenever the chains do not interact with each other dynamically, E is the osmotic compressibility (for a related discussion of the interpretation of the modulus in the context of entangled Θ solutions, see ref 5). Explicit examples clarifying the meaning of E are given in the Appendix.

It is expedient to write E in terms of ν, the effective number of dynamic units per unit volume making up the rubbery network (or associated with an osmotic compressibility when the chains are disentangled dynamically):

$$E \equiv k_B T \nu \tag{3}$$

where k_B is Boltzmann's constant and T is the temperature. On eliminating the unknown time scale τ, we have from eqs 1–3

$$X \equiv \Delta\eta D_s / k_B T \simeq \nu R^2 \tag{4}$$

The empirical quantity X (dimension: length^{-1}) has the following features: (a) X is independent of the detailed dynamics of an individual chain. We expect its properties to be more universal than the experimental quantities η and D_s themselves. (b) X is a quasi-static variable which may be simpler to understand than τ. (c) X is probably much less sensitive to changes in chain configuration than η and D_s.

In the Appendix we show explicitly the (theoretical) usefulness of eq 4 by applying it to polymer solutions conforming to the usual theories postulating a mechanism for the chain dynamics (Rouse, reptation, Kirkwood–Riseman).

In practice we expect two important limiting cases for the quantity X: (i) It is independent of the molar mass M. This implies that ν is inversely proportional to M so the chains themselves form the individual units within the transient network. (ii) X is proportional to M. Hence ν is independent of M so the effective units are intensive quantities. We note that when either case occurs, it is an important consistency check on the dynamic scaling hypothesis.

Experimental Section

Technique. Chain self-diffusion coefficients were measured by the use of pulsed field gradient nuclear magnetic resonance (PFG-NMR).[6] Shear viscosities were determined with a Haake Rotovisco RV20 viscosimeter with shear rates in the range 1–300 s^{-1}. Measurements were performed at T = 298 K. A detailed description of the experimental setup has been given before.[7,8]

Chemicals. *Sodium poly(styrenesulfonate)* fractions were obtained from Pfannenschmidt, Hamburg, and were manufactured at the Pressure Chemical Co., Pittsburgh, PA. Three degrees of polymerization were studied: PSS31 with N = 169 (M_w = 31 000), PSS88 with N = 481 (M_w = 88 000), and PSS177 with N = 967 (M_w = 177 000). Polydispersity ratios (M_w/M_n) were found to be smaller than 1.2 by gel permeation chromatography. Polyelectrolyte solutions were prepared in Millipore water. D_s was determined in a concentration range of 0.02–0.5 monoM; η in a concentration range of 0.001–0.5 monoM (the unit of concentration monoM refers to the molarity of the monomeric units). For the fraction PSS177, D_s and η were also determined in solutions with added NaCl concentrations of 0.01 and 0.1 M. We note that at low concentrations (c_p < 0.03 monoM) the experimental accuracy of D_s is limited. NaPSS sample preparation has been described in detail before.[7] A detailed account of the NaPSS measurements is given in refs 7, 8, and 18.

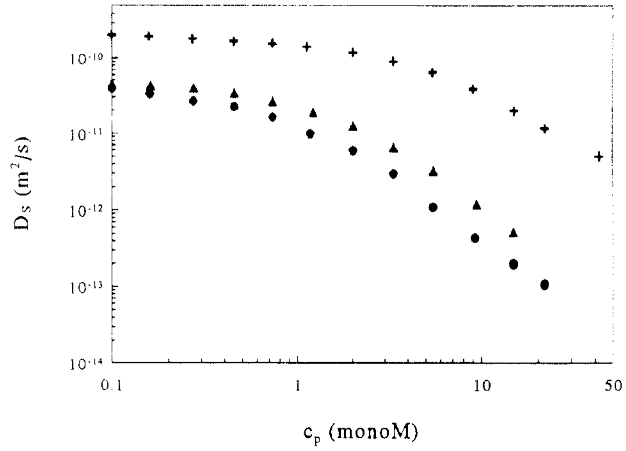

Figure 1. Poly(ethylene oxide) in D_2O. Chain self-diffusion for various degrees of polymerization: (+) PEO15; (▲) PEO200; (●) PEO350.

Poly(ethylene oxide) fractions were obtained from Merck. Three degrees of polymerization were studied: PEO15 with N = 34 (M_w = 1500), PEO200 with N = 455 (M_w = 20 000), and PEO350 with N = 795 (M_w = 35 000). The fractions were characterized by gel permeation chromatography in 0.1 M KNO_3 on a Waters Model ALC/GPC equipped with Toyo Soda TSK-PW columns (G3000 PW 30 for $M_w \leq$ 20 000; G5000 for $M_w >$ 20 000). M_w/M_n ratios were found to be 1.04, 1.10, and 1.15 for PEO15, PEO200, and PEO350, respectively. The PEO was dissolved in D_2O (Merck), allowing 3 days for equilibration. Concentrations were in the range of 0.1 monoM up to 42 monomol/kg solvent. Solutions were stored in the dark at 4 °C to minimize biological and photochemical degradation. Experimental conditions and setups were the same as those in the NaPSS experiments. Echo attenuation plots in the PFG-NMR experiments showed simple exponential decays, as expected for homogeneous diffusion[6] in samples of monodisperse fractions. No shear rate dependence of the viscosity was found, allowing simple determination of the zero shear viscosity η. At very high concentrations experimental accuracy is limited.

Poly(ethylene oxide) Results

The concentration dependence of the self-diffusion and viscosity is presented in Figures 1 and 2 on a log–log scale. Clearly, no simple scaling relations are evident for these transport properties as a function of the concentration. However, some indication for a transition is apparent in the region between about 1 and 5 monoM.

In Table Ia–c we give values of X calculated from D_s and η using eq 4, and they are plotted against the concentration in Figure 3. It is seen that the quantity X is independent of the molar mass within experimental accuracy over two decades of concentration. Furthermore, X does show scaling behavior as a function of the concentration with exponent 0.72(±0.03). Note that the scaling is not valid in the entire region but breaks down at very high concentrations.

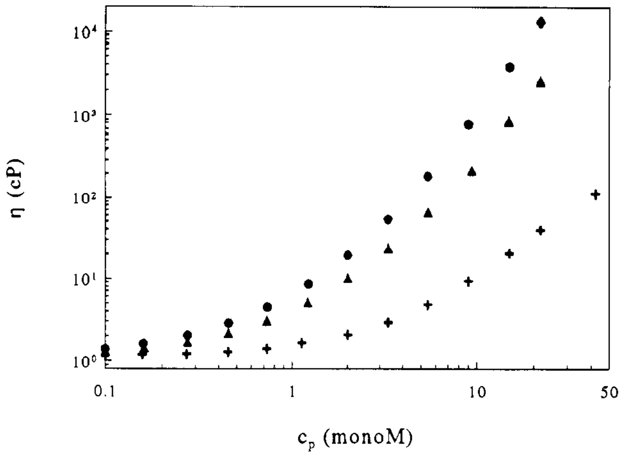

Figure 2. Poly(ethylene oxide) in D_2O. Zero shear viscosity η for various degrees of polymerization: (+) PEO15; (▲) PEO200; (●) PEO350.

Discussion of PEO Results

If we assume the density remains invariant and the PEO monomer has a radius and length of 0.3 nm, the PEO volume fraction ranges from 0.14% to about 60%. In addition, the overlap concentration c^* of the chains is lower than 10^{-1} monoM for all the samples. Consequently, the PEO solutions that have been studied here are either semidilute or concentrated.

Dependence on Molar Mass. The fact that X is independent of the molar mass enables us to hypothesize that the individual chains form the elastic units in both the semidilute and concentrated regimes up to about 10 monoM. Apparently, local entanglements are not effective within the transient network, that is, as far as the *dynamic* properties are concerned. Figures 4 and 5 show that simple scaling relations are not possible to describe the mass dependences of η and D_s when considered individually. However, we may define concentration ranges in which the diffusion coefficient can be normalized to M^α with α varying from -0.75 to -2 or larger. For reasons stated earlier, the consideration of these individual curves is outside the scope of this paper.

Concentration Dependence. Since the chains are the independent elastic units in the transient network, the quantity ν should be proportional to c, the number of chains per unit volume. It is then concluded from eq 4 that $R^2 \sim c^{-0.28\pm0.03}$. Since water is a good solvent for PEO,[9] the chains are swollen in dilute solution. The concentration dependence of R therefore amounts to an increasingly effective screening of the intramolecular excluded volume with increasing concentration. The exponent of -0.28 ± 0.03 agrees well with the prediction -0.25 of classical semidilute scaling theory for good athermal solvents.[1] Remarkably, the scaling approach seems to predict the correct concentration dependence of R^2 even in the concentrated regime where volume fractions are on the order of tens of percent. In the latter regime a one-parameter scaling theory is not deemed to be applicable.

Additional Remarks. With respect to the behavior of the disentanglement time τ and underlying mechanistic features we note the following.

(a) The screening length is the basic intensive scale in the scaling theory for the description of entangled polymeric solutions at low volume fraction.[1] Though we find that the concentration dependence of R^2 is well described by this theory, the density of independent elastic units as introduced in the theoretical section is not an intensive quantity for aqueous PEO solutions. We conclude that the relevant length scale associated with the elastic driving force for chain dynamics cannot always be inferred simply from the static description, as is often assumed in scaling theory.[1]

(b) Since local entanglements are ineffective in the global dynamics of the chain, the effective medium of chains surrounding a test chain is isotropic on average and on a time scale of τ, even at very high concentrations. Locally, however, chain motion may be *anisotropic*. In particular, at segment concentrations higher than b^{-3}, the inverse volume of revolution of a Kuhn segment of length b, the reorientation of a test segment may be significantly hindered by the presence of other segments. We denote the corresponding transition by $c^{**} \equiv b^{-3}$. The concentration regime above c^{**} is sometimes called *concentrated*.[2] In the case of PEO, c^{**} is equal to about 1 monoM (1.5%) using a value for the Kuhn length of 1.2 nm.[10] Accordingly, it is tempting to identify the crossover in the concentration dependence of D_s and η as a c^{**} transition from the semidilute to the concentrated regime. (See Figures 1 and 2.)

(c) Because the chains themselves are the basic dynamic units, the behavior of τ is reflected in the concentration dependence of the specific viscosity $\eta_{sp} \equiv \Delta\eta/c_p$, as can be inferrred from eq 2. In effect, the quantity $\Delta\eta/ck_BT$ is proportional to τ and is plotted in Figure 6. It is seen that up to about 0.5 monoM, it hardly varies with the polymer concentration. Beyond the c^{**} transition, however, τ increases strongly with concentration. We know there are no local entanglements involved in the osmotic force (proportional to E or ν) driving the solution to equilibrium when the PEO solution is perturbed. Yet, apparently, the global motion of a chain (i.e. on a time scale τ) is somehow connected to the local hindrance of Kuhn segments. This connection is unclear at present.

Increased hindrance of local reorientations above c^{**} has also been observed in the nuclear magnetic relaxation of PEO nuclei.[11] A significant increase of the relaxation rates of chain deuterons at high concentration could be explained in terms of a strong slowing down of the segmental reorientation when the persistence length exceeds the average distance between contact points of neighboring chains.

Although the global chain dynamics is affected by the crossover from the semidilute to the concentrated regime, the quantity X does *not* show a transition at c^{**}, as can be seen from Figure 3. This is in accordance with the supposition mentioned earlier, that details of the dynamics will be reflected in the principal relaxation time τ rather than in X.

Poly(styrenesulfonate) Results

In Table IIa–e we present the self-diffusion coefficient D_s and the viscosity increment $\Delta\eta$ at zero shear, together with the quantity X calculated from eq 4. In Figure 7, X is plotted against the monomer concentration for several NaPSS fractions. We discern that X is independent of the molar mass to a good approximation. Up to a concentration of about 0.2 monoM, X is proportional to $c_p^{0.50\pm0.01}$. Moreover, the addition of 0.01 M NaCl does not affect X within experimental accuracy.

The influence of a substantial amount of salt (c_s = 0.1 M NaCl) is shown in Figure 8. Evidently, X now follows an enhanced concentration dependence. The dotted line in Figure 8 represents $X \sim c_p^{0.64}$. Since experimental accuracy is limited at low concentrations ($c_p < 0.04$ monoM), this line must be viewed as approximate, merely serving as a guide to the eye. The dependence of X at concentrations higher than about 0.1 monoM is weaker

Table I. Zero Shear Viscosity Increment, Chain Self-Diffusion Coefficient, and X versus Monomer Concentration

c_p (monoM)	$\Delta\eta$ (cP)	$10^{11}D$ (m^2/s)	10^4X (Å^{-1})	c_p (monoM)	$\Delta\eta$ (cP)	$10^{11}D$ (m^2/s)	10^4X (Å^{-1})
(a) PEO15							
0.100	0.06	20.7	3.1	3.33	1.85	9.05	40.1
0.158	0.10	19.8	5.0	5.45	3.73	6.45	57.6
0.269	0.12	18.4	5.4	9.02	8.27	3.85	76.3
0.449	0.19	17.0	7.7	14.88	19.34	1.99	92.3
0.729	0.31	15.8	11.7	21.66	38.53	1.16	107.1
1.13	0.56	14.3	19.1	42.22	112.8	0.5	135.2
2.01	0.98	12.0	28.3				
(b) PEO200							
0.10	0.23	4.50	2.4	2.01	9.07	1.27	27.6
0.16	0.36	4.27	3.6	3.33	22.53	0.66	35.4
0.27	0.61	4.00	5.9	5.48	66.05	0.33	51.5
0.45	1.08	3.40	8.8	9.41	223.3	0.12	63.7
0.73	1.99	2.63	12.6	14.74	871.0	0.05	108.6
1.22	4.03	1.90	18.3				
(c) PEO350							
0.10	0.29	3.95	2.7	2.01	18.2	0.60	26.2
0.16	0.52	3.31	4.2	3.33	53.4	0.30	38.3
0.27	0.94	2.65	6.0	5.46	186.1	0.11	48.4
0.45	1.77	2.22	9.4	9.03	792.4	0.044	83.3
0.73	3.41	1.63	13.3	14.88	3909	0.020	190.0
1.23	7.50	1.00	17.9	21.60	13479	0.011	351.5

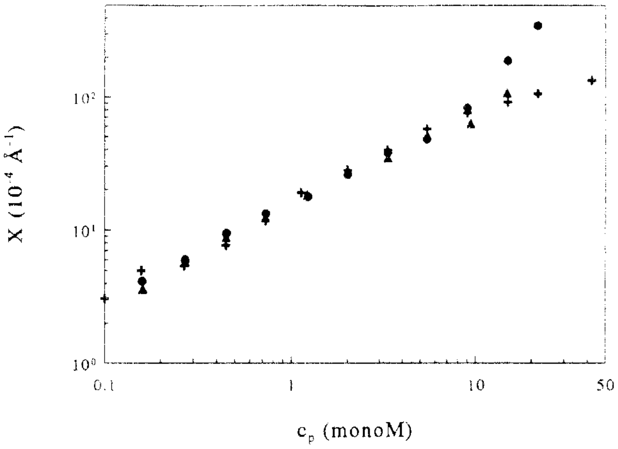

Figure 3. Poly(ethylene oxide) in D_2O. The quantity X for various degrees of polymerization: (+) PEO15; (▲) PEO200; (●) PEO350.

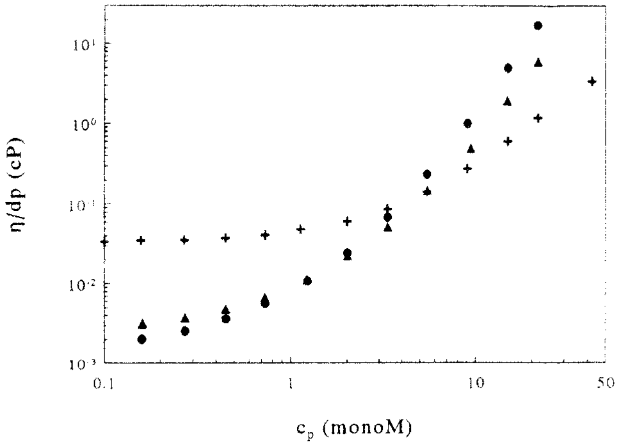

Figure 4. Poly(ethylene oxide) in D_2O. η over degree of polymerization vs c_p for various degrees of polymerization: (+) PEO15; (▲) PEO200; (●) PEO350.

than the exponent of 0.64 would indicate and curves asymptotically toward the salt-free value of 0.5.

Discussion of PSS Results

In the following analysis of the NaPSS results, we will assume that a direct transposition is possible from polymer to polyelectrolyte systems in the sense that generic

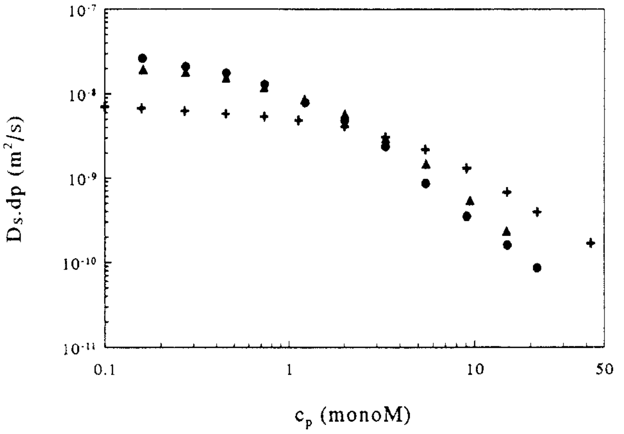

Figure 5. Poly(ethylene oxide) in D_2O. D_s times degree of polymerization vs c_p for various degrees of polymerization: (+) PEO15; (▲) PEO200; (●) PEO350.

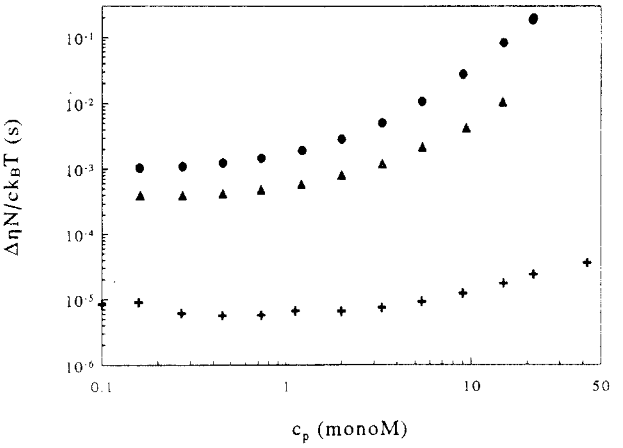

Figure 6. Poly(ethylene oxide) in D_2O. The principal relaxation time τ proportional to $\Delta\eta N/ck_BT$: (+) PEO15; (▲) PEO200; (●) PEO350.

polymeric features remain invariant despite introducing electrostatic interactions in the system.[12,13] In particular, since we are dealing with intrinsically flexible polyelectrolytes at concentrations which are not exceptionally low, we expect that $R^2 \sim M$ to a good approximation.

Salt-Free Systems. Dependence on Molar Mass. Because X does not depend on the molar mass, we conclude that the chains behave as independent elastic units (see

Table II. Zero Shear Viscosity Increment, Chain Self-Diffusion Coefficient, and X versus Monomer Concentration

c_p (monoM)	$\Delta\eta$ (cP)	$10^{11}D$ (m^2/s)	10^4X (Å^{-1})	c_p (monoM)	$\Delta\eta$ (cP)	$10^{11}D$ (m^2/s)	10^4X (Å^{-1})
			(a) PSS31 (No Added Salt)				
0.250	1.72	2.95	12.4	0.049	0.57	3.70	5.2
0.161	1.33	3.20	10.4	0.036	0.47	3.80	4.4
0.110	1.04	3.51	8.9	0.022	0.35	4.10	3.5
0.070	0.74	3.65	6.6				
			(b) PSS88 (No Added Salt)				
0.250	4.99	0.98	11.9	0.049	1.72	1.35	5.7
0.163	3.72	1.14	10.3	0.035	1.44	1.34	4.7
0.110	2.97	1.24	9.0	0.021	1.12	1.22	3.3
0.074	2.23	1.28	7.0	0.014	0.89	1.07	2.3
			(c) PS177 (No Added Salt)				
0.437	16.66	3.35	13.6	0.105	5.80	5.44	7.7
0.384	14.72	3.47	12.4	0.097	5.29	5.60	7.2
0.295	11.94	3.86	11.2	0.073	4.44	5.80	6.3
0.233	10.07	4.30	10.5	0.072	4.65	5.86	6.6
0.217	9.48	4.64	10.7	0.048	3.47	6.10	5.1
0.178	8.3	4.92	9.9	0.047	3.62	6.40	5.6
0.150	7.32	4.98	8.9	0.036	3.17	6.50	5.0
0.146	6.88	5.10	8.5	0.035	3.00	6.30	4.6
0.125	6.51	5.27	8.3	0.027	2.83	6.30	4.3
			(d) PSS177 (C_s = 0.01 M)				
0.497	21.99	2.91	15.6	0.159	7.31	5.20	9.2
0.437	19.10	3.03	14.1	0.123	5.83	5.86	8.3
0.383	16.71	3.23	13.1	0.098	5.12	6.37	7.9
0.300	13.09	3.73	11.9	0.085	4.09	6.58	6.5
0.234	10.38	4.48	11.3	0.052	2.57	8.85	5.5
0.207	9.17	4.77	10.6	0.040	2.00	9.80	4.8
			(e) PSS177 (C_s = 0.1 M)				
0.389	13.99	4.55	15.6	0.261	8.39	6.14	12.5
0.348	12.04	4.93	14.4	0.216	6.49	6.99	11.0
0.304	9.94	5.51	13.3	0.174	4.89	8.21	9.8

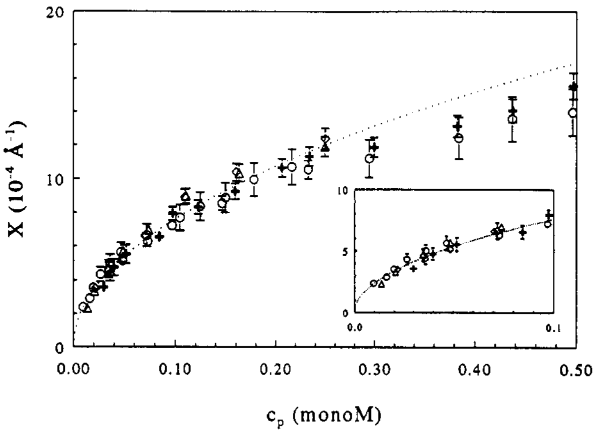

Figure 7. Poly(styrenesulfonate) in water. The scaling variable X for various degrees of polymerization. Salt free: (◇) PSS31, (△) PSS88, (○) PSS177. c_s = 0.01 M: (+) PSS177. The dotted line represents a power fit with exponent 0.5. In the inset the concentration regime between 0 and 0.1 monoM is expanded.

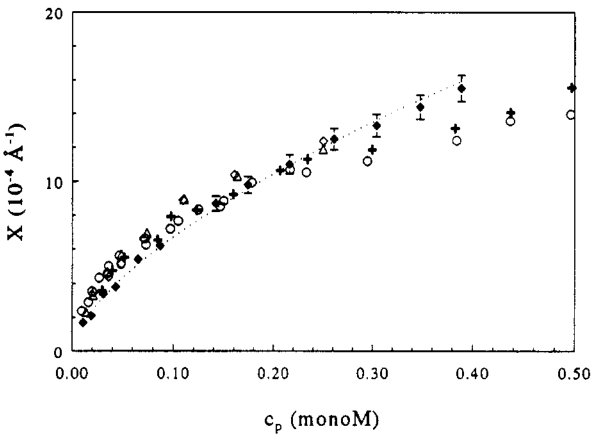

Figure 8. Poly(styrenesulfonate) in water. The scaling variable X vs the concentration c_p. Symbols are as in Figure 8 but together with results for PSS177 in 0.1 M NaCl (◆). The dotted line represents $X \sim c_p^{0.64}$ and serves as a guide to the eye.

theoretical section). A transient network consisting of local entanglements is an ineffective model for the global dynamics of NaPSS chains in salt-free solutions.

Concentration Dependence. A precise analysis of the concentration dependence of X for polyelectrolytes is much more difficult than in the case of neutral polymers, since the Kuhn segment length, the segment interactions, and the segment friction all depend on the ionic strength. Furthermore, electrohydrodynamic dissipation due to the strong coupling of counterion flow with the motion of the polyelectrolyte network is very poorly understood. Nevertheless, some progress can be made.

To account for additional contributions to the dissipation in polyelectrolyte solutions, we introduce a dimensionless function h_1 in the expression for the viscosity increment

$$\Delta\eta \simeq h_1 E \tau \qquad (5)$$

It is reasonable to assume h_1 depends on the monomer concentration but not on the molar mass. In effect, the electrostatic interactions are local.

Since we find that $\nu \sim M^{-1}$, we naturally assume that in salt-free solutions the deformation of *single* chains determines the elastic response. Hence, we write:

$$\nu \simeq \frac{c}{N} h_2 \qquad (6)$$

with h_2 a dimensionless function depending on c and describing a possible electrostatic contribution, $c = c_p N_{av} 10^3$ the monomer concentration of dimension m^{-3}, c_p the usual monomer concentration in monoM (10^3 mol·m^{-3}), and N_{av} Avogadro's number.

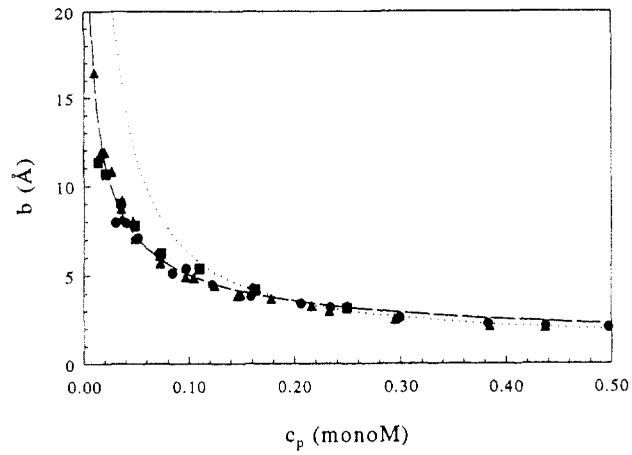

Figure 9. Poly(styrenesulfonate) in water. Kuhn segment length b vs the concentration c_p as determined from X. Zero additional dissipation ($h = 1$). Salt free: (♦) PSS31, (■) PSS88, (▲) PSS177. $c_s = 0.01$ M: (●) PSS177. The dotted line represents the curve $b = b_0 + b_1/c_p$ with $b_0 = 0.9(\pm0.1)$ Å and $b_1 = 0.6(\pm0.1)$ Å·mol·L^{-1}. The dashed line represents $b = b_1/c_p^{1/2}$ with $b_1 = 1.6(\pm0.1)$ Å·mol·L^{-1}.

We further suppose that the static conformation of the polyelectrolyte chains is essentially wormlike and Gaussian. The mean square end-to-end distance of a long ideal wormlike chain is given by

$$R^2 \simeq bL \tag{7}$$

where b is the Kuhn segment length equal to twice the total persistence length L_t[14] and L is the chain length. Note that we completely disregard excluded volume effects like those conjectured above c^{**}.[13] From the definition for X (eq 4) and eqs 3 and 5–7, we have

$$X \simeq hbac = hbac_pN_{av}10^3 \tag{8}$$

with a the monomer length ($a_{PSS} = 2.5$ Å). The dimensionless function $h \equiv h_1h_2 = h(cl^3)$ where l is a length scale which itself is a function of other microscopic length scales (see below).

In order to analyze the concentration dependence of X we next adopt two different scenarios depending on the type of starting assumption. Obviously, they are meant to be illustrative only.

(i) Additional Dissipation May Be Neglected, i.e. $h \equiv 1$. Persistence Length. The concentration dependence of the total persistence length L_t is then readily determined from X. The values for the Kuhn segment length $b = 2L_t$ as calculated from eq 8 are given in Figure 9 as a function of the concentration. From $X \sim c_p^{0.5}$ it follows that $b \sim c_p^{-0.5}$ for concentrations up to about 0.2 monoM. We next assume that the intrinsic and electrostatic contributions to the chain stiffness are additive, that is, $b = b_0 + b_e(c_p)$. The Kuhn segment length will approach the intrinsic Kuhn segment length b_0 at high ionic strength: $b_e(c_p) \downarrow 0$ for large c_p. At higher concentrations, the dependence of the Kuhn segment length is best represented by the form $b = b_0 + b_1/c_p$ given the experimental accuracy. This is shown in Figure 10. The best fit gives $b_0 = 0.9(\pm0.1)$ Å and $b_1 = 0.6(\pm0.1) \times 10^{-12}$ mol·m^{-2}. The intrinsic Kuhn segment length of poly(styrenesulfonate) is 24 Å.[15] Our value of b_0 implies a prefactor of about 25 in the scaling relation for X. The origin of this relatively large prefactor is not yet understood. The value of $25b_1 = 0.15 \times 10^{-10}$ mol·m^{-2} is to be compared with the theoretically calculated value $b_1^{calc} = 2/(16Q\pi aN_{Av}10^3)$ (mol·m^{-2}).[16,17] In water at room temperature the Bjerrum length $Q = 7$ Å and $b_1^{calc} = 3.8 \times 10^{-10}$ mol·m^{-2}. In Figure 11 the corrected persistence lengths and the calculated persistence lengths[16,17] are given as a function of the concentration.

Principal Relaxation Time. Since the chains are the independent elastic units and $h \approx 1$, the concentration dependence of τ can be represented by plotting $N\Delta\eta/k_BTc$ versus c_p. The result is depicted in Figure 12 for PSS177. For concentrations smaller than approximately 0.05 monoM, we have $\tau \sim c_p^{-0.5}$. In the concentration regime between 0.05 and about 0.2 monoM τ is virtually independent of the polyelectrolyte concentration.

(ii) Analysis Using a Specific Model for the Persistence Length. The ansatz $h \cong 1$ may be unrealistic. To make headway, we next let the Kuhn segment length vary with the ionic strength as follows:[16,17]

$$b = b_0 + \frac{b_1}{\kappa^2} \tag{9}$$

in which b_1 is a constant equal to $1/2Q$ and κ is the inverse Debye screening length. This model was developed to describe the electrostatic stiffening of a single polyelectrolyte chain in the local stiffness approximation ($\kappa L_T \gg 1$).[13] In Figure 13 we show the Kuhn length according to eq 9 where the screening from uncondensed counterions is also taken into consideration.[13] End effects are not accounted for in the present analysis.

Elasticity Modulus E and the Function h. We first determine the concentration dependence of the product h_1E from X using eqs 4, 5, 7, and 9 which is shown in Figure 14 for PSS177. Next, Figure 15 exhibits the concentration dependence of the function h which is evaluated from eqs 8 and 9. For $c_p < 0.05$ monoM, it is found that h increases with concentration. For c_p larger than about 0.2 monoM, h decreases with concentration.

Principal Relaxation Time τ. By using the scaling relation (1) for the self-diffusion coefficient and eqs 7 and 9, we ascertain the concentration dependence of the principal relaxation time τ shown in Figure 16 for the fraction PSS177. Similarly to the first scenario, for concentrations smaller than 0.2 monoM, τ increases strongly with *de*creasing concentration. For c_p larger than 0.2 monoM, the relaxation time increases with the concentration only slightly.

Systems with Added Salt. We have to know the dependence of X on the molar mass in order to establish the nature of the elastic response. Owing to time limitations we have been able to determine X for only one sample (PSS177) with added salt. (However, we have managed to verify that the mass dependence of D_s is not very strong in a similar concentration regime[18].) Nevertheless, Figure 8 proves that the addition of even 0.1 M NaCl merely shifts the $X(c_p)$ curve with respect to the scaling curve valid at zero salt. This implies the mechanism behind the elastic response is modified a bit at most, so it is reasonable to assume the individual chains remain the elastic units.

$C_s = 0.01$ M. The behavior of X is indistinguishable from that of salt-free solutions down to concentrations as low as 0.02 monoM. By contrast, the constitutive quantities D_s and η start deviating from those for salt-free NaPSS at concentrations as high as 0.2 monoM.[18] This value is what one would expect from a consideration of uncondensed counterions (the effective ionic strength of a 0.2 monoM salt-free NaPSS solution is $0.2a/2Q \simeq 0.03$ monoM, so it is increased a bit by the addition of 0.01 M NaCl). The invariance of $X(c_p)$ between 0.02 and 0.2 monoM is remarkable because we know the excluded volume effect and the functions h_1 and h_2 should be sensitive to added salt.

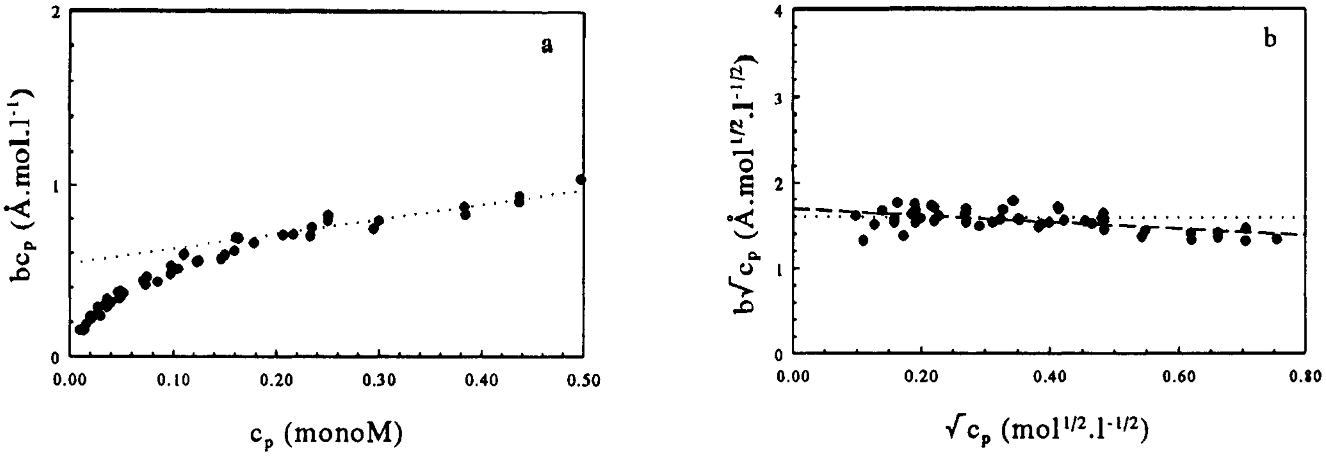

Figure 10. Poly(styrenesulfonate) in water. (a) Scaled Kuhn length bc_p vs the concentration c_p. The dotted line represents a linear fit $bc_p = b_0c_p + b_1$ with $b_0 = 0.9(\pm0.1)$ Å and $b_1 = 0.6(\pm0.1)$ Å·mol·L^{-1}. (b) $bc_p^{1/2}$ vs $c_p^{1/2}$. The dotted and dashed lines represent linear fits $bc_p^{1/2} = b_0c_p^{1/2} + b_1$ with $b_0 = -0.01(\pm0.05)$ Å, $b_{1.} = 1.6(\pm0.1)$ Å·mol$^{1/2}$·L$^{-1/2}$ and $b_0 = -0.4(\pm0.1)$ Å, $b_{1.} = 1.7(\pm0.2)$ Å·mol$^{1/2}$·L$^{-1/2}$, respectively.

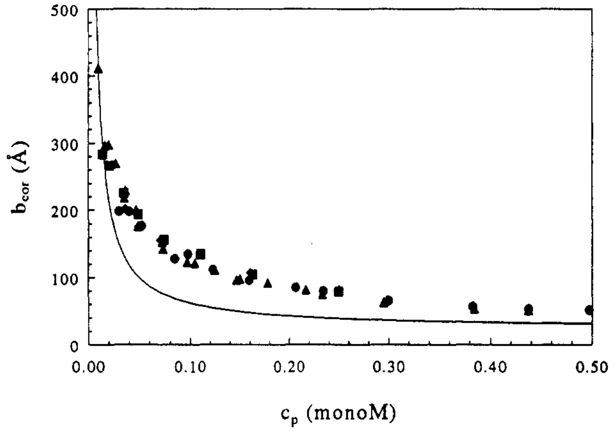

Figure 11. Poly(styrenesulfonate) in water. Corrected Kuhn segment length b_{cor} vs c_p. Zero additional dissipation ($h = 1$). The solid line is the Kuhn length according to eq 9.

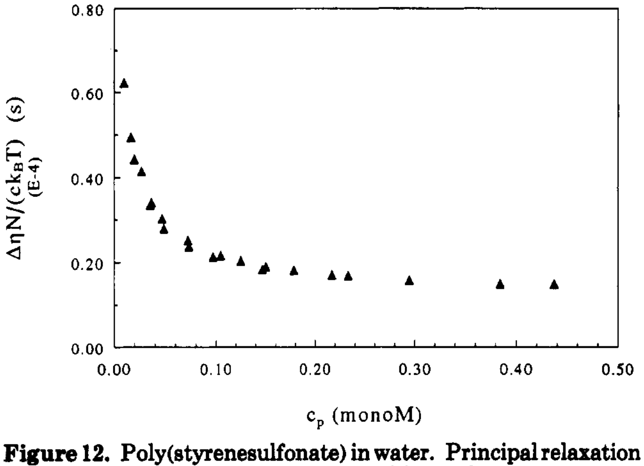

Figure 12. Poly(styrenesulfonate) in water. Principal relaxation time τ proportional to $N\Delta\eta/c_pk_BT$ for PSS177. Salt free (scenario I, zero additional dissipation ($h = 1$)).

***C_s* = 0.1 M.** Electrostatic screening is now effective under excess salt conditions (or almost so). We than recover basically the neutral polymer case, so it is plausible to set $h_1 \cong 1$ and $h_2 \cong 1$, since they are now independent of the concentration. The volume fraction of NaPSS is quite low, so we can use classic scaling analysis for semidilute polyelectrolytes.[13] The relation $R^2 \sim c_p^{-1/4}$ then implies $X \sim c_p^{3/4}$ which is close to the experimental form $X \sim c_p^{0.64}$. Remnant uncondensed counterions would tend to lower the exponent $^3/_4$ a bit. Hence, the difference between the two exponents is not worrisome.

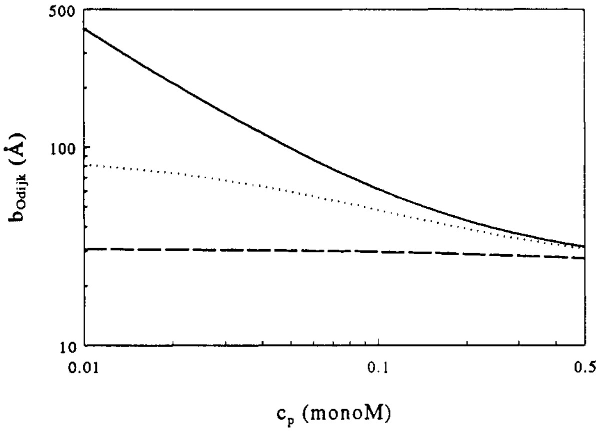

Figure 13. Poly(styrenesulfonate) in water. Theoretical values for the Kuhn segment length as a function of c_p calculated according to eq 9: (solid) salt free; (dashed) c_s = 0.01 M; (dotted) c_s = 0.1 M.

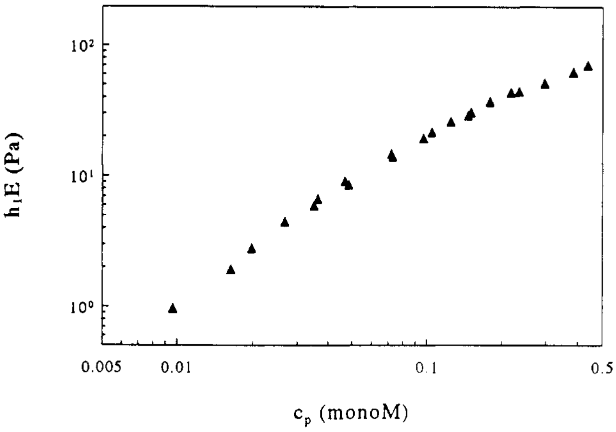

Figure 14. Poly(styrenesulfonate) in water. Elasticity modulus times the function h_1 as determined from X for PSS177. Salt free (scenario II).

Additional Remarks

(a) Local entanglements appear to be ineffective in the global dynamics of NaPSS chains in salt-free solutions. In both scenarios τ starts to increase significantly with decreasing polyelectrolyte concentration for c_p smaller than about 0.15 monoM. This behavior of τ is reflected in several dynamic features.[7] In addition, it is expected that shear thinning effects become more pronounced with decreasing concentration which is borne out by experiment.[19]

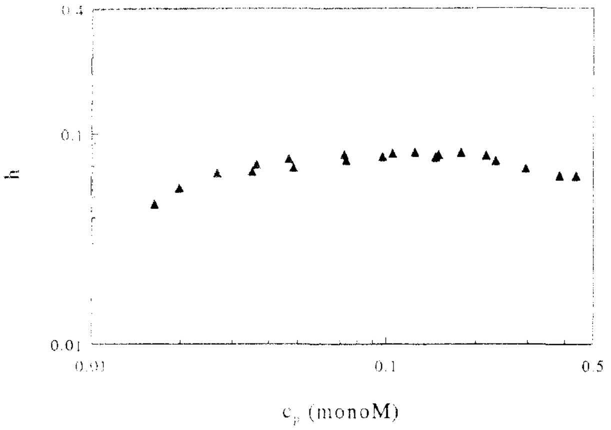

Figure 15. Poly(styrenesulfonate) in water. The function h vs c_p for PSS177. Salt free (scenario II).

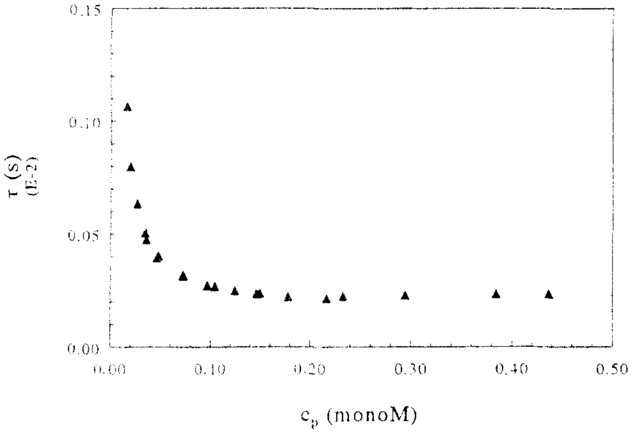

Figure 16. Poly(styrenesulfonate) in water. Principal relaxation time calculated from the self-diffusion coefficient assuming ideal chain conformations. Salt free (scenario II).

Tentatively, we identify a crossover when the persistence length is of the same order of magnitude as the average distance between contact points of neighboring chains. This transition was first proposed in a static scaling analysis of semidilute salt-free systems and denoted by c^{**}.[13] Note that the behavior of salt-free solutions of NaPSS with *decreasing* concentration resembles the behavior of PEO in water with *increasing* concentration (which was reported in the previous section). This paradoxical disparity arises because electrostatic screening changes dramatically with the polyelectrolyte concentration.[13]

(b) It is quite remarkable that the curve $X(c_p)$ is almost universal, i.e. independent, even of the charge! The two scaling forms (Figure 3 (PEO) and Figure 8 (NaPSS with and without added salt)) are quite close to each other.

Concluding Remarks

We have shown that our dynamic scaling hypothesis can be confirmed purely on empirical grounds. In fact, for both PEO and salt-free NaPSS, the quasi-static quantity X proves to be independent of the molar mass whereas the viscosity and the self-diffusion exhibit complex mass dependences. In both cases, the chains themselves form the individual elastic units involved in the elastic response just after a slight perturbation of the solution away from equilibrium. We can draw additional conclusions only by making further suppositions of a less general nature. We have outlined several *possible* scenarios for charged and uncharged systems although we have purposely refrained from discussing detailed mechanisms for the dynamics of the chains. Despite this limited objective, we hope this work will lead to more insight into macromolecular dynamics.

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Appendix

The scaling hypothesis yielding eq 4 is consistent with four disparate dynamical theories.

(I) Kirkwood–Riseman. For a dilute solution of linear flexible polymers of concentration c, the number of Kuhn segments per unit volume, we have in the nondraining limit[14]

$$\Delta\eta \simeq \eta_0 c R^3/N \qquad \text{(A1)}$$

$$D_s \simeq k_B T/\eta_0 R \qquad \text{(A2)}$$

where N is the number of Kuhn segments in a chain. Equation 4 gives

$$\nu \equiv c/N \qquad \text{(A3)}$$

i.e. ν is to be identified with the number of chains per unit volume, as it should, for in dilute solution the individual chains are the dynamic units and E is the osmotic compressibility.

(II) Rouse Dynamics. For instance, in a concentrated polymer solution the viscosity η is much greater than η_0. From Doi and Edwards (≡DE) we have[2]

$$\eta \simeq \Delta\eta \simeq c\zeta R^2 \quad \text{(DE 7.33)} \qquad \text{(A4)}$$

$$D_s \simeq \frac{k_B T}{N\zeta} \quad \text{(DE 4.31)} \qquad \text{(A5)}$$

where ζ is the friction coefficient of a Kuhn segment. Hence, from eq 4 we should have

$$\nu \equiv c/N \qquad \text{(A6)}$$

which is again the number of chains per unit volume. Indeed, in the Rouse model the chains themselves form the individual dynamic units in the transient gel.

(III) Reptation in a concentrated polymer solution ($\eta \gg \eta_0$)

$$\eta \simeq \Delta\eta \simeq N^3\zeta b^2 c(b/a)^4 \quad \text{(DE 7.43, 7.46, 7.47)} \qquad \text{(A7)}$$

$$D_s \simeq k_B T a^2/N^2\zeta b^2 \quad \text{(DE 6.40)} \qquad \text{(A8)}$$

where b is the Kuhn length and a is the diameter of the effective tube. Equation 4 yields

$$\nu \equiv cb^2/a^2 \qquad \text{(A9)}$$

which is precisely the number of segments between two dynamic entanglements per unit volume in view of the fact that the entanglement number $N_e \equiv a^2/b^2$.

(IV) Blob Model for Semidilute Solutions. This is a rescaled version[1] of the reptation model (III). From eq 4 we would have ν identical with the number of blobs between dynamic entanglements per unit volume.

In conclusion, the empirical quantity X is a direct probe of the effective density of dynamic entanglements or units within four different theoretical frameworks.

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