Scaling Behavior of the High-Frequency Dielectric Properties of Poly-L-lysine Aqueous Solutions

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ABSTRACT: We report the scaling behavior of the dielectric parameters, the dielectric strength $\Delta\epsilon$ and the relaxation time τ, of the high-frequency dielectric dispersions observed in aqueous solutions of poly-L-lysine of different molecular weights, from 4000 to 167 000. The dielectric properties have been measured in the frequency range from 1 MHz to 1.8 GHz, and the dispersions have been attributed to internal motions of side chain polar groups, resulting in an intermediate relaxation process between that due to the counterion atmosphere polarization and that due to the orientational polarization of the water molecules. The scaling relationships are compared with the predictions of the dynamic scaling theory recently surveyed by Dobrynin, Colby, and Rubinstein (*Macromolecules* **1995**, *28*, 1859) developed to describe both the dilute and semidilute regimes of aqueous polyelectrolyte solutions. Our data, based on the analysis of a new set of dielectric measurements of poly-L-lysine aqueous solutions over an extended range of polymer concentrations and temperatures for each of the molecular weights investigated, are qualitatively consistent with this scaling picture. Deviations from the predicted indices in the power law behavior of the relaxation time in the high molecular weight polymer solutions are briefly discussed.

Introduction

The dynamics of dilute and semidilute aqueous polyelectrolyte solutions markedly differs from that of uncharged polymers, owing to strong electrostatic interactions existing between different polymer chains or between different regions of the same chain, which lead, depending on the polyion concentration, to different chain conformations.

Recently, Dobrynin et al.,[1,2] generalizing the scaling picture proposed by de Gennes et al.,[3] Odijk,[4,5] and Pfeuty[6] for the conformation of a charged flexible polymer chain, have surveyed and extended this theory to dynamic scaling in both dilute and semidilute solutions and have developed simple scaling laws to describe some dynamic properties of polyelectrolyte solutions. Depending on the polymer chain conformation, the existence of different regimes has been postulated, ranging from highly dilute solutions, where the polyion chains are hydrodynamically isolated from one another and interact via long-range unscreened Coulombic potential, to more concentrated solutions, where chains overlap and interact.

In salt-free solutions, these different regimes, occurring in different concentration intervals and being governed by different length scales, i.e., the electrostatic blob size D and the correlation length ξ_0, can be summarized as follows. For dilute concentration regimes ($c < c^*$, c^* being the overlap concentration at which the distance between chains equals the end-to-end distance R), the screening length r_B is larger than the distance R_M between chains, polyions interact, and the polymer conformation is that of an extended (rodlike) chain of electrostatic blobs. At higher concentrations ($c > c^*$), the electrostatic screening length r_B is approximately equal to the correlation length ξ_0, but larger than the Debye length $1/K_D$, and the chain is a random walk of correlation blobs.[1,2] For each of these regimes, a different behavior of the polymer dynamics is expected, reflecting, for example, different frequency-dependent dielectric and conductometric properties of the whole polymer solution.

In fact, dielectric relaxation spectroscopy is a well-estabilished tool to investigate the dynamic properties of charged polyions in aqueous solutions, where, at low frequencies, the counterion atmosphere polarization reflects the conformational properties of the whole polyion chain or, at higher frequencies, the micro-Brownian dynamics, attributable to internal motion of the side chain polar groups, results in a further relaxation process. This technique gives useful information on the details of the electrostatic interactions occurring in the whole system.

Owing to the structural complexity of a polyelectrolyte solution, the dielectric spectra of these systems generally display multiple relaxation processes, depending on the frequency of the applied electric field.

In this work, we have measured the high-frequency dielectric behavior of poly-L-lysine aqueous solutions over an extended range of polymer concentrations (up to 12 mg/mL), and we have analyzed the dependence of the dielectric parameters (the dielectric strength $\Delta\epsilon$ and the relaxation time τ) on the polymer concentration c, according to the scaling picture proposed by Dobrynin et al.[1,2] For both the regimes investigated (dilute and semidilute solutions), power laws describing the dependence on concentration of the dielectric strength and relaxation time have been evidenced, and the values of the power law exponents have been discussed on the basis of the scaling behavior. A generally good agreement has been found, and deviations, when they have occurred, have been discussed as probably due to a

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crossover between two contiguous concentration regimes.

Review of the Scaling Theory

In this section, we briefly review, using the notation of Dobrynin et al.,[1,2] the scaling approach recently proposed by these authors to describe the dynamics of dilute and semidilute flexible polyelectrolyte aqueous solutions.

The polyelectrolyte solution contains charged flexible polyions built up of N monomers of size b, each of them carrying an ionizable group of charge $|z_p|e$ and a counterion of charge $|z_1|e$, z_p and z_1 being their valences, respectively. The polymer solution contains c monomers per unit volume. Owing to counterion condensation in highly charged polyelectrolyte systems,[7−9] a fraction of counterions will condense on the polyion so that $Q_{tot} = (N/A)e$ is the effective total charge (incorporating the counterion condensation) on a single chain. Here, A is the number of monomers per effective charge, after condensation takes place.

In very dilute solutions, the Debye screening length $1/K_D$ is larger than the distance R_M between chains, and because of charge interaction via unscreened Coulombic potential, each polyion can be represented as an extended chain of length L composed of N/g_e electrostatic blobs of size D and charge $q_D = (g_e/A)e$. Here, g_e is the number of monomers inside an electrostatic blob. In the dilute regime, at a polymer concentration larger than the concentration at which the chain becomes flexible, when the electrostatic screening length $r_B \approx (B/cb)^{1/2}$ is smaller than the chain size R, the polyions are self-avoiding walks of electrostatically screened blobs of size r_B, each of which is an extended configuration of electrostatic blobs of size D, and the end-to-end distance can be written as[1,2]

$$R \approx b^{2/5}B^{-2/5}N^{3/5}c^{-1/5} \qquad (1)$$

In eq 1, B is the ratio of the chain contour length Nb to the length L. When the polymer concentration is increased and the distance R_M between chains equals their end-to-end length R, a different regime appears. The overlap concentration c^* is given by[1,2]

$$c^* \approx N/L^3 \approx B^3b^{-3}N^{-2} \qquad (2)$$

At polymer concentrations larger than c^*, since the electrostatic and the excluded volume interactions are screened on a length scale larger than the correlation length ξ_0, the chain is a random walk of correlation blobs. The chain is composed of $N_\xi = N/g$ correlation blobs of size $\xi_0 \approx (B/cb)^{1/2}$, each of them containing g monomers and carrying electric charge $q_{\xi_0} = (g/A)e$. In this concentration regime, the end-to-end polyion length is given by[1,2]

$$R \approx \xi_0 {N_\xi}^{1/2} \approx (b/B)^{1/4}N^{1/2}c^{-1/4} \qquad (3)$$

As the concentration is further increased, this regime shifts toward a concentrated region.

The main parameters describing the dielectric dispersion are the dielectric strength $\Delta\epsilon = \epsilon_s - \epsilon_\infty$ and the relaxation time τ. To evaluate these parameters, the appropriate dynamics of the polymer chain must be known. As pointed out by Muthukumar,[10] in the dilute regime ($c < c^*$), Zimm dynamics is applicable,[11] whereas in the semidilute unentangled regime ($c > c^*$), where hydrodynamic interactions are screened, the Rouse model is appropriate.[11] Within this context, the relaxation time can be viewed as proportional to the hydrodynamic volume of the chain, according to

$$\tau \approx \eta_s R^3/K_B T \qquad (4)$$

and the dielectric strength proportional to the concentration of polarizable objects times the square of the dipole moment and hence to the square of the screening length r_B, according to the expression

$$\Delta\epsilon \approx c{r_B}^2 \approx cR^2 \qquad (5)$$

In dilute solutions, the polarizable object is part of the chain inside the electrostatic screening length r_B, resulting in the dependence given in eq 5. With the dependence of R on c given by eq 1 (dilute regime, $c < c^*$), the dielectric parameters scale as

$$\tau \approx c^{-3/5} \approx c^{-0.6} \qquad (6)$$

$$\Delta\epsilon \approx c^{3/5} \approx c^{0.6} \qquad (7)$$

If the polymer chain is highly flexible, the electrostatic nature of the excluded volume effect should be taken into account. In this case, the end-to-end distance R of a single chain in the infinite dilution limit is given by[4]

$$R \approx (Nb)^{3/5}{L_t}^{1/5}{K_D}^{-1/5} \qquad (8)$$

where L_t, the total persistence length, is defined as the sum of the electrostatic persistence length $L_e = l_B/(4\pi {K_D}^2A^2)$ and the intrinsic persistence length L_p[4,5,12,13]

$$L_t = L_e + L_p \qquad (9)$$

and K_D is the inverse of the Debye screening length

$$K_D = (4\pi l_B c/A)^{1/2} \qquad (10)$$

In the limit of $L_p \ll L_e$, valid for an electrostatic blob chain, the end-to-end distance R scales with the polymer concentration c (concentration of the monomeric units) like

$$R \approx c^{-3/10} \qquad (11)$$

This dependence yields the following scaling laws for the dielectric increment $\Delta\epsilon$ and the relaxation time τ:

$$\Delta\epsilon \approx cR^2 \approx c^{2/5} \approx c^{0.4} \qquad (12)$$

$$\tau \approx R^3 \approx c^{-9/10} \approx c^{-0.9} \qquad (13)$$

In the semidilute regime ($c > c^*$), the hydrodynamic interactions between correlation blobs are screened, and the motion of the whole chain, described by the Rouse model,[11] is characterized by relaxation time

$$\tau \approx \frac{\eta_s {\xi_0}^3 N^2}{K_B T g^2} \approx \frac{\eta_s N^2}{K_B T} c^{-1/2}\left(\frac{b}{B}\right)^{3/2} \qquad (14)$$

However, if the dynamics inside the correlation blob is considered, where motions of different sections of the chain are strongly hydrodynamically coupled just as in the dilute regime, the relaxation time inside the correlation blob is Zimm-like (eq 4)

$$\tau \approx \eta_s \xi_0^{\,3}/K_B T \qquad (15)$$

where R is substituted with the correlation blob size ξ_0. The dependences on the concentration c are given by

$$\tau \approx c^{-0.5} \qquad (16)$$

in the Rouse-like dynamics and

$$\tau \approx c^{-1.5} \qquad (17)$$

in the Zimm-like dynamics.

In both the above cases, the dielectric strength, resulting from a polarization on length scales of the order of the correlation length ξ_0, becomes

$$\Delta\epsilon \approx (c/g)\xi_0^{\,3} \approx c\xi_0^{\,2} \qquad (18)$$

With the dependence of ξ_0 on c, the dielectric strength scales with the concentration c as

$$\Delta\epsilon \approx c^0 \qquad (19)$$

It must be noted that the above-stated dependences of the dielectric strength and the relaxation time on the polymer concentration are generally justified on the basis of dynamical processes occurring along the polymer chain, rather than on the basis of the side chain dynamics. However, a correlation between these two dynamics due to cooperativity effects and to strong coupling between internal motion of polar side groups and that of the polymer backbone has been postulated. In other words, the dynamics of side chains necessarily involves the dynamics of the backbone, resulting in a "local dynamics" of the polymer chain, since no time scale separation exists between "internal" and "overall" motion.[14,15] Further support of this hypothesis comes from high-frequency dielectric properties of aqueous solutions of different polyamino acids. We have recently investigated[16] the high-frequency dispersions of poly-γ-glutamate that differs from poly-α-glutamate in the length of the side chains, since the glutamic acid residues are linked in the main chain through γ-carbonyl groups. In this case, we observed that relaxation times of poly-γ-glutamate are larger than those of poly-γ-glutamate, which corresponds to a more extended side chain, indicating that the micro-Brownian dynamics is deeply influenced by the backbone conformation.

Similar indications have been put forward by Mashimo et al.,[17,18] who found that the relaxation time of poly-α-glutamate aqueous solutions, associated with the side chain motion, increases with the degree of helix content in the polymer chain, suggesting a correlation between motion of the coiled repeat units and that of neighboring chains. A more recent investigation carried out by the present authors on the same system,[19] even if discussed in a somewhat different context, confirms the presence of an increasing relaxation time as a more rigid chain prevails.

According to these indications, the ansatz that the dependence of the dielectric parameters $\Delta\epsilon$ and τ associated with the side chain dynamics on polymer concentration c could be similar to that occurring in the dynamics of the whole chain or inside a different section of the chain (correlation blobs) seems reasonable, and on the basis of this assumption, we will discuss our experimental findings about the high-frequency dielectric properties of poly-L-lysine aqueous solutions and compare our results with the scaling theory.

Experimental Section

The dielectric properties (permittivity $\epsilon'(\omega)$, dielectric loss $\epsilon''(\omega)$, and low-frequency electrical conductivity $\sigma(0)$) have been obtained by means of frequency domain dielectric spectroscopy measurements, using a radio-frequency impedance analyzer, Hewlett-Packard model 4291A. The measured complex reflection coefficients (modulus $|\rho|$ and phase angle ϕ), caused by a coaxial line partially filled with the sample to be investigated, have been converted into the dielectric parameters by means of a bilinear equation relating the reflection coefficients and the complex dielectric constants of three different standard liquids.[20] We employed as reference liquids three NaCl electrolyte solutions at different appropriate molarities, to completely cover the electrical conductivity interval experienced by our samples. The details of this procedure are described elsewhere.[16]

Four different samples of poly-L-lysine (PLys) were obtained from Sigma Chemical Co. The molecular weights reported by the manufacturer were 4000, 18 000, 100 000, and 167 000. All the solutions were prepared at the desired concentration (within the range from $C = 0.5$ mg/mL to $C = 12$ mg/mL) with Q-quality water (Millipore), whose electrical conductivity was less than $(1-2) \times 10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$ at 20 °C. The pH of the solutions, in the whole polymer concentration and temperature interval investigated, varied between 7.8 and 8.0. At these pH values, the polymer is fully ionized and behaves as a polyelectrolyte with a monovalent charged group per monomer, with monomer length $b = 3.4$ Å. In aqueous solutions, according to the Manning counterion condensation theory,[7−9] condensation occurs since the charge parameter $\xi = e^2/\epsilon K_B T$ is larger than the critical value $\xi_c = 1/z_p z_1$.

Results and Discussion

The dielectric properties of poly-L-lysine aqueous solutions in the frequency range from 1 MHz to 1.8 GHz have been measured for polymers of different molecular weights (from 4000 to 167 000) in the temperature range from 5 to 50 °C. The polymer concentration has been varied from 0.5 to 12 mg/mL, to cover the dilute and semidilute concentration regimes, depending on the polyion molecular weight.

For all the samples studied, in the frequency range investigated, a well-characterized dielectric dispersion occurs, located between a dispersion at lower frequencies, attributed to fluctuation of partially condensed counterions along the polymer backbone, and a further dispersion at higher frequencies due to the orientational polarization of the water molecules.

The interpretation of this intermediate dispersion has long been controversial. We have attributed the observed dispersion in these and in similar polymer solutions to the dynamics of side chain motion. Investigations of the influence of the internal dynamics on the dielectric properties of poly-α-glutamic acid,[16,21] of charged and uncharged comblike derivatives of chitosan[22,23] and of poly-L-lysine of different degrees of ionization[19] have also been reported by the present authors, in recent years.

The deconvolution of the whole dielectric spectrum of an aqueous polyelectrolyte solution into its components when more than one dispersion occurs is in general a difficult task. In this case, the problem is further complicated by the fact that the low-frequency dispersion falls below the frequency interval investigated and that only the low-frequency tail of the water molecule orientational polarization may be observed with our experimental setup.

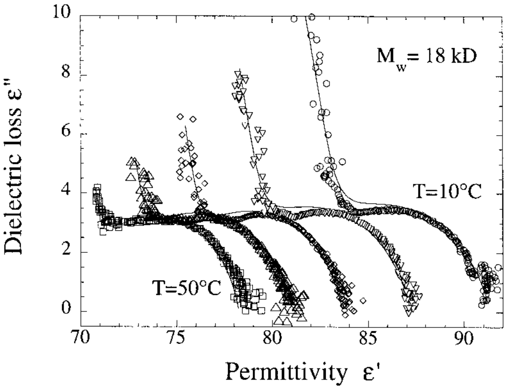

Figure 1. A Cole–Cole plot of aqueous solutions of poly-L-lysine at some selected temperatures, from 10 to 50 °C. The polymer molecular weight is $M_w = 18\,000$, and the polymer concentration is $C = 5.6$ mg/mL. The full lines are the calculated values according to eq 20.

Consequently, we have analyzed the observed spectra on the basis of the Cole–Cole[24] relaxation function

$$\epsilon^*(\omega) - \epsilon_\infty = \epsilon'(\omega) - i\epsilon''(\omega) - \epsilon_\infty = \frac{\Delta\epsilon}{[1 + (i\omega\tau)^\beta]} + \frac{\epsilon_\infty - \epsilon_{\infty\ H_2O}}{1 + i\omega\tau_{H_2O}} \qquad (20)$$

to which a Debye-type dispersion function has been added (characterized by dielectric increment $\Delta\epsilon_{H_2O} = \epsilon_\infty - \epsilon_{\infty\ H_2O}$ and relaxation time τ_{H_2O}) to take into account the contribution of the water molecule polarization. Here $\Delta\epsilon$, τ, and ϵ_∞ are the dielectric strength, the relaxation time, and the high-frequency permittivity, respectively, of the side chain dynamics dispersion and ω is the angular frequency of the applied electric field.

To have a first, rough localization of the relaxation frequency of the dispersion associated with the internal motion of the side chain polar groups, we have performed a multiple-step fitting procedure based on the Marquardt algorithm for complex functions.[25] Since the shape of the dielectric loss spectrum $\epsilon''(\omega)$ strongly depends on the value of the low-frequency conductivity $\sigma(0)$ to be subtracted from the total loss $\sigma(\omega)/\epsilon_0\omega$, we have made a preliminary simultaneous fit of $\epsilon'(\omega)$ and the total loss $\sigma(\omega)/\epsilon_0\omega$, with five free parameters, $\Delta\epsilon$, τ, β, ϵ_∞, and $\sigma(0)$, with the only constrain that all parameters should be >0. The value of the parameter $\sigma(0)$ thus obtained is then subtracted from the measured conductivity $\sigma(\omega)$, the dielectric loss $\epsilon''(\omega)$ is evaluated, and a new set of parameters from the simultaneous fit of both the permittivity $\epsilon'(\omega)$ and the dielectric loss $\epsilon''(\omega)$ are now obtained. This procedure is iterated until a reasonable minimization (judged from the value of χ^2) is reached. In this way, the simultaneous fit of the real part $\epsilon'(\omega)$ and the imaginary part $\epsilon''(\omega)$ strongly reduces the contribution to the overall dielectric dispersion due to the high-frequency tail of the lower frequency process and of the low-frequency tail of the higher frequency process. A typical result is shown in Figure 1, where the dielectric dispersions at some selected temperatures from 10 to 50 °C are represented by means of a Cole–Cole plot. As can be seen, the usual semicircular arc is followed, at higher frequencies, by a further relaxation process, indicating the beginning of the dispersion of the aqueous phase.

To compare experiments with the expected scaling behavior described by eqs 6 and 7 (or by eqs 12 and 13) in the dilute regime and by eqs 16 and 17 in the semidilute regime, the overlap concentration c^* defined by eq 2 must be evaluated. This concentration depends on the parameter B that, depending on the quality of the solvent, can be written, in our case, as

$$B \approx (A^2 b/l_B)^{2/3} \qquad (21)$$

where $l_B = e^2/(\epsilon K_B T)$ is the Bjerrum length, $K_B T$ the thermal energy, and ϵ the permittivity of the aqueous phase. Assuming B on the order of 4–5, we obtain values of c^* corresponding to values well above the maximum concentration investigated for samples of low molecular weights ($M_w = 4000$ and $M_w = 18\,000$), corresponding to a value of about 4–5 mg/mL for the sample with molecular weight $M_w = 100\,000$, and finally corresponding to a value of about 0.5–1 mg/mL for the sample with molecular weight $M_w = 167\,000$. Since the scaling relationship that defines the crossover concentration deals with an unknown prefactor, but on the order of unity, the above values must be considered as a rough estimate of the concentration dependence of the different polymer conformational regimes.

Table 1. Scaling Indices *m* and *n* in the Concentration Dependence of the Dielectric Parameters Δϵ (Index *m*) and τ (Index *n*) of Poly-L-lysine Aqueous Solutions

	experimental values		expected values	
M_w	$\Delta\epsilon \approx c^m$	$\tau \approx c^n$	$\Delta\epsilon \approx c^m$	$t \approx c^n$
		Dilute Regime ($c < c^*$)		
4000	0.52 ± 0.08			
			0.6 (eq 7)	−0.6 (eq 6)
18 000	0.36 ± 0.03	−0.54 ± 0.04		
			0.4 (eq 12)	−0.9 (eq 13)
100 000	0.15 ± 0.02	−0.85 ± 0.02		
		Semidilute Regime ($c > c^*$)		
100 000	0.08 ± 0.02	−0.50 ± 0.05		−0.5 (eq 16)
			0 (eq 19)	
167 000	0.08 ± 0.03	−0.85 ± 0.02		−1.5 (eq 17)

However, on the basis of this evaluation, samples with molecular weight $M_w = 4000$ and $M_w = 18\,000$ behave as a dilute solution ($c < c^*$), the sample with molecular weight $M_w = 167\,000$ is in the semidilute regime ($c > c^*$), and an intermediate regime occurs in the sample of molecular weight $M_w = 100\,000$, where the crossover concentration c^* falls within the concentration range investigated (for the sample of molecular weight $M_w = 100\,000$, c^* corresponds to a concentration of about $C = 4$–5 mg/mL).

The analysis of the scaling behavior of the dielectric parameters as a function of concentration is shown in Figures 2–6, according to the concentration regime investigated. As can be seen, the relaxation time τ and the dielectric strength $\Delta\epsilon$ undergo a scaling behavior with well-defined scaling exponents. The experimental values and those expected on the basis of the scaling laws are collected in Table 1.

Figure 2 shows the scaling of the dielectric increment $\Delta\epsilon$ with the concentration C (C is proportional to the concentration c through the relation $C = cM_w/NN_A$, N_A being the Avogadro number) at some selected temperatures for the samples in the dilute regime ($M_w = 4000$ and $M_w = 18\,000$). The curves have a slope of 0.52 ± 0.08 for poly-L-lysine of molecular weight $M_w = 4000$ and 0.36 ± 0.03 for poly-L-lysine of molecular weight $M_w = 18\,000$, not too far from the values expected from eq 7, $\Delta\epsilon \approx c^{0.6}$, or from eq 12, $\Delta\epsilon \approx c^{0.4}$, if the electrostatic contribution to the persistence length is taken into account.

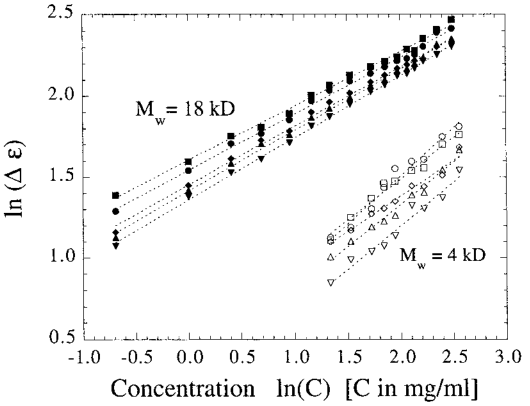

Figure 2. Scaling behavior of the dielectric strength $\Delta\epsilon$ in the dilute regime ($c < c^*$) of poly-L-lysine aqueous solutions, for two different molecular weights. $M_w = 4000$: (□) $T = 10$ °C; (○) $T = 20$ °C; (◇) $T = 30$ °C; (△) $T = 40$ °C; (▽) $T = 50$ °C. $M_w = 18\,000$: (■) $T = 10$ °C; (●) $T = 20$ °C; (◆) $T = 30$ °C; (▲) $T = 40$ °C; (▼) $T = 50$ °C. The dotted lines are the fitted power law dependences.

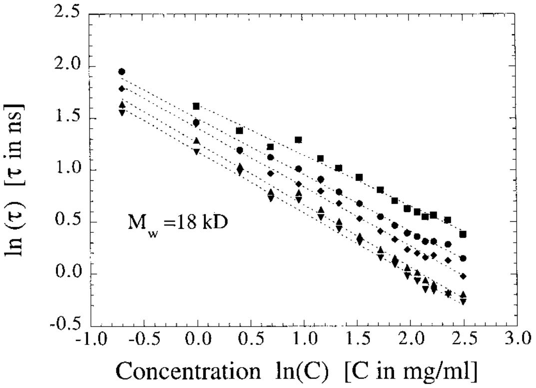

Figure 3. Scaling behavior of the relaxation time τ in the dilute regime ($c < c^*$) of poly-L-lysine aqueous solutions, for molecular weight $M_w = 18\,000$: (■) $T = 10$ °C; (●) $T = 20$ °C; (◆) $T = 30$ °C; (▲) $T = 40$ °C; (▼) $T = 50$ °C. The dotted lines are the fitted power law dependences.

Similarly, the relaxation times for molecular weight $M_w = 18\,000$ (Figure 3) scale with an index (-0.54 ± 0.04) in good agreement with the prediction $\tau \approx c^{-0.6}$ (eq 6), suggesting that the electrostatic contributions could not be relevant. As far as the relaxation times of the polymers of molecular weight $M_w = 4000$ are concerned, we must remark that, particularly in the low-concentration range, the observed dielectric dispersions are generally very small (of about one or two dielectric units) and the deconvolution procedure yields the dielectric parameters (particularly the relaxation time) with very large uncertainties, preventing the evaluation of an appropriate scaling law.

As the molecular weight is increased, there is a progressive shift from the dilute to semidilute regime. A typical example is given by the sample of molecular weight $M_w = 100\,000$, where, as we have above stated, the crossover concentration falls at about $C = 4-5$ mg/mL. In the dilute regime ($c < c^*$), the dielectric increment scales as $\Delta\epsilon \approx c^{0.15\pm0.02}$ and the relaxation time as $\tau \approx c^{-0.85\pm0.02}$. In this case, these indices differ from those expected on the basis of eqs 6 and 7 (in the absence of electrostatic contributions), but, on the contrary compare reasonably well with predictions from scaling behavior, taking into account the electrostatic nature of the persistence length effect. In fact, this effect produces a scaling behavior described by $\Delta\epsilon \approx c^{0.4}$ and $\tau \approx c^{-0.9}$ (eqs 12 and 13), with indices close to those observed experimentally. The agreement is very good for the relaxation time and a little worse for the dielectric increment. These indications suggest that the electrostatic contribution becomes progressively more relevant as the molecular weight increases and the flexibility of the chain becomes important.

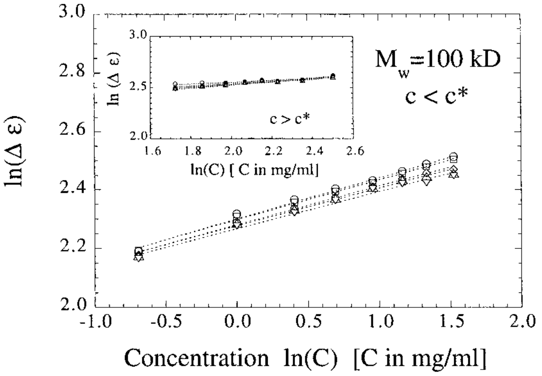

Figure 4. Scaling behavior of the dielectric strength $\Delta\epsilon$ in the dilute regime ($c < c^*$) for aqueous solutions of poly-L-lysine of molecular weight $M_w = 100\,000$ at some selected temperatures: (□) $T = 10$ °C; (○) $T = 20$ °C; (◇) $T = 30$ °C; (△) $T = 40$ °C; (▽) $T = 50$ °C. The dotted lines are the fitted power law dependences. The inset shows the scaling behavior in the semidilute regime ($c > c^*$).

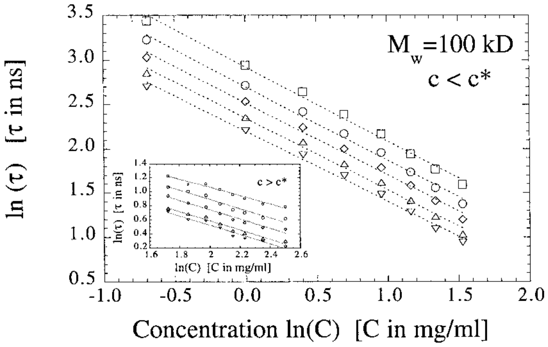

Figure 5. Scaling behavior of the relaxation time τ in the dilute regime ($c < c^*$) for aqueous solutions of poly-L-lysine of molecular weight $M_w = 100\,000$ at some selected temperatures: (□) $T = 10$ °C; (○) $T = 20$ °C; (◇) $T = 30$ °C; (△) $T = 40$ °C; (▽) $T = 50$ °C. The dotted lines are the fitted power law dependences. The inset shows the scaling behavior in the semidilute regime ($c > c^*$).

In the semidilute regime ($c > c^*$), we observe scaling laws $\Delta\epsilon \approx c^{0.08\pm0.02}$ and $\tau \approx c^{-0.50\pm0.05}$, in very good agreement with predictions (eqs 19 and 16). These dependences for the sample with molecular weight $M_w = 100\,000$ are shown in Figures 4 and 5.

For the highest molecular weight investigated ($M_w = 167\,000$), in the semidilute regime ($c > c^*$), we observe scaling behaviors described by $\Delta\epsilon \approx c^{0.08\pm0.02}$ and $\tau \approx c^{-0.85\pm0.02}$ (Figure 6). Whereas the scaling of the dielectric strength is consistent with the expected independence of the polymer concentration, $\Delta\epsilon \approx c^0$ (eq 19), the scaling of the relaxation time deviates from that predicted by the Rouse model ($\tau \approx c^{-0.5}$, eq 16), and this index is more consistent with the expectation based on a dilute behavior ($\tau \approx c^{-0.9}$), increasing toward the value -1.5 (eq 17, Zimm-like dynamics inside the correlation length ξ_0). Analogously to the dilute regime, this finding could suggest the presence of a crossover regime governed by the ratio of some typical chain size to the total polymer

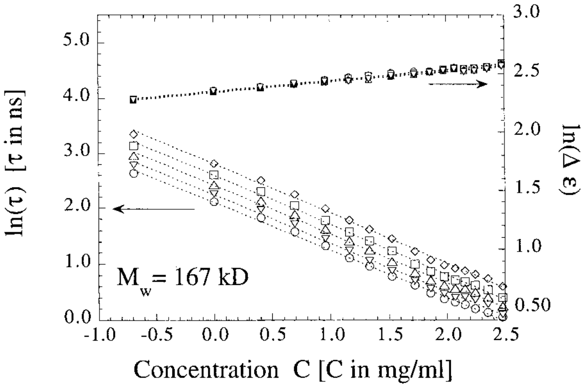

Figure 6. Scaling behavior of the dielectric strength $\Delta\epsilon$ and the relaxation time τ in the semidilute regime ($c > c^*$) for aqueous solutions of poly-L-lysine of molecular weight M_w = 167 000 at some selected temperatures: (◇) $T = 10$ °C; (□) $T = 20$ °C; (△) $T = 30$ °C; (▽) $T = 40$ °C; (○) $T = 50$ °C. The dotted lines are the fitted power law dependences.

chain length, where in the dilute regime this size equals the persistence length with or without the electrostatic contribution and, in the semidilute regime, the correlation blob size.

Some general comments are in order. It must be noted that the scaling exponents are only valid in the limit as the degree of polymerization tends to infinity, i.e., when an asymptotic regime is reached. In the present case, nevertheless the molecular weights investigated are not too large, the experimental findings show that a scaling law behavior holds, suggesting that, at least to a first approximation, the above analysis is reasonable. In the semidilute regime, for moderate to high molecular weights, the relaxation time τ shows a concentration dependence of $\tau \approx c^{-0.85\pm0.02}$, and it is surprising that this law continues to work even above the overlap concentration c^*. The same dependence has been seen in the apparent viscosity of sulfonated polystyrene solutions with no added salt by Boris and Colby,[26] who suggest that this dependence is likely a universal feature of polyelectrolyte systems. In this concentration regime, the phenomenological slope fit of the dielectric strength (indices 0.08 ± 0.02 for both samples with molecular weights M_w = 100 000 and M_w = 167 000) is consistent with the predictions of the scaling theory that the semidilute dielectric strength should be independent of concentration. Taking into account the uncertainties due to the deconvolution of the dielectric spectra, the agreement we have found is satisfactorily good. A little larger disagreement appears in the indices of the dielectric strength scaling in dilute solutions of smaller molecular weight polyions. This can be due both to the difficulty in the deconvolution of the dielectric spectra in the presence of dielectric dispersions of small strengthes and to a lesser flexibility of the chain in polyions of small or moderate molecular weight.

In conclusion, the concentration dependence of both the dielectric strength $\Delta\epsilon$ and the relaxation time τ of the dielectric dispersions of poly-L-lysine aqueous solutions centered at about 100−500 MHz and attributed to the local dynamics of side chain polar groups is in reasonable agreement with the scaling behavior recently proposed by Dobrynin et al.[1,2] for both the dilute and semidilute polymer concentration regimes. However, some deviations are found in the relaxation time of the higher molecular weight polyions (in the semidilute regime) that scales with a higher power of concentration ($\tau \approx c^{-0.85\pm0.02}$) than that predicted by Rouse-type dynamics. This deviation can be justified taking into account the ratio of the correlation blob size to the length of the whole chain. When the correlation length is comparable with the polymer length, the local dynamics is coupled to that of the whole chain, whereas when ξ_0 is smaller than R, the coupling between the local dynamics and that of the backbone inside the correlation blob predominates (eq 17). The importance of the dynamics within the correlation blobs in the transport properties of aqueous polyelectrolyte solutions have been recently discussed by us[27] and in a more general context for semidilute polymer solutions by Nicolai et al.[28]

Finally, it must be noted that similar power laws in the dependence of the dielectric parameters (the dielectric strength and the relaxation time) on the polyion molecular weight M_w, as well as other polyelectrolyte parameters (correlation length ξ, electrostatic blob size, and screening length) should apply. Recently, Muthukumar[10,29] studied in detail the different dynamics of a polyelectrolyte chain by considering three different kinds of screening lengths, associated with electrostatic, excluded volume, and hydrodynamic interactions, and the various power laws for the electrophoretic mobility, diffusion coefficient, and viscosity have been derived. In particular, in semidilute solutions and at the low salt limit, it has been found that the screening length ξ is proportional to $c^{-1/2}$. The ansatz that the observed relaxation time is proportional to ξ results in a power law dependence on c with exponent −0.5, which is the same as that of eq 16 and is exactly the value we observe in the semidilute sample (M_w = 100 000). However, the present data do not allow this analysis to be extended to other parameters depending on the molecular weight since, for each concentration regime, where different indices are expected, we have investigated samples of only two different molecular weights, thus preventing any meaningful determination of the exponents in the power law behaviors. The dielectric investigations should be extended to more concentrated polyion solutions and over a wider molecular weight interval to evaluate the possible influence of a crossover region between semidilute and concentrated regimes and establish the experimental dependence on the molecular weight and on other characteristic lengths.

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