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Viscoelastic Properties of Polyelectrolyte Solutions. 1. Zero-Shear Viscosity

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ABSTRACT: Zero-shear viscosity η^0 of polyelectrolyte solutions was measured in the absence and presence of added salt. Samples used were poly(*N*-methyl-2-vinylpyridinium chloride)s having 6.94×10^5, 1.10×10^6, and 2.73×10^6 for the weight-average molecular weight. It was found that the polymer concentration dependence of η^0 in semidilute regions increases with an increase in the concentration of added salt and almost agrees with that for nonionic polymers in good solvents at high concentrations of added salt. These features can be explained by the reptation model assuming that the correlation length related to entanglements is determined by electrostatic interaction evaluated from Donnan equilibrium at the respective concentration of added salt.

Introduction

Linear viscoelastic properties of polymers in the terminal region can be discussed in terms of two parameters representing energy dissipation and storage, such as zero-shear viscosity η^0 and steady-state compliance J_e, respectively. η^0 of nonionic polymer solutions can be understood by classifying the solutions as at least three regions, i.e., dilute, semidilute, and concentrated regions, depending on concentration C and the degree of the coil overlapping C/C^*, where C^* is defined as[1,2]

$$C^* = 3M/(4\pi\langle S^2\rangle^{3/2}N_A) \qquad (1)$$

where M and $\langle S^2\rangle$ are the molecular weight and the mean-square radius of gyration of the polymer at infinite dilution and N_A is Avogadro's number.

In dilute regions, the reduced zero-shear viscosity $\eta^0{}_R$ defined as $\eta^0{}_{sp}/C[\eta]$ is expressed in expansion forms as

$$\eta^0{}_R = 1 + k'C[\eta] + ... \qquad (2a)$$

$$\eta^0{}_R = 1 + k(C/C^*) + ... \qquad (2b)$$

where $\eta^0{}_{sp} = (\eta^0 - \eta_s)/\eta_s$, η_s is the solvent viscosity, k' is Huggins' constant, $k = 3k'\Phi'/4N_A$, and $[\eta]$ is the intrinsic viscosity. Here, the second equation is obtained by using the Flory–Fox equation, $[\eta] = \Phi'\langle S^2\rangle^{3/2}/M$ where Φ' is the Flory viscosity factor.

In semidilute regions, $\eta^0{}_R$ is given in the following scaling form by assuming that $\eta^0{}_{sp} \propto M^{3.4}$ in entangled regions:[3-5]

$$\eta^0{}_R \propto (C/C^*)^{(4.4-3\nu)/(3\nu-1)} \qquad (3a)$$

$$\eta^0{}_R \propto (C[\eta])^{(4.4-3\nu)/(3\nu-1)} \qquad (3b)$$

where ν is the exponent in the relationship between the mean-square radius of gyration and molecular weight, $\langle S^2\rangle \propto M^{2\nu}$. Here, the second equation is also obtained by using the Flory–Fox equation. Thus, $\eta^0{}_R$ can be expressed as universal functions of C/C^* or $C[\eta]$, eqs 2 and 3, from dilute through semidilute regions, if the molecular weights of the samples are high enough.

On the other hand, η^0 of polyelectrolyte solutions have been studied mainly in dilute regions, and their intrinsic viscosities were discussed in terms of expansion factors[6] if the ionic strength is not lower than 0.01, while the studies on the frequency dependence of viscoelastic properties demonstrate that the relaxation time which cannot be ascribed to the Zimm theory is dominant in the terminal region, at the lower ionic strength.[7,8] If finite concentrations where coil overlapping becomes significant, a few studies have been reported,[9-11] but the samples had relatively broad molecular weight distributions, and/or the ranges of polymer concentration were limited.

In a previous paper, we reported the preparation of a polyelectrolyte sample with relatively narrow molecular weight distributions over a wide range of molecular weight.[12] In the present work, therefore, we measured η^0 of the polyelectrolyte samples at finite concentrations in the absence and presence of added salt and studied the effect of electrostatic interactions on η^0 in comparison with η^0 of nonionic polymer solutions.

Experimental Section

Samples. Polyelectrolytes used were poly(*N*-methyl-2-vinylpyridinium chloride)s (PMVP-Cl) with narrow molecular weight distributions. They were prepared by quaternizing anionically polymerized poly(2-vinylpyridine)s with dimethyl sulfate in dimethylformamide and by dialyzing the aqueous sample solution against aqueous NaCl solutions. The weight-average molecular weight M_w was measured by a light scattering method, and its ratio to the number-average molecular weight M_w/M_n was determined by GPC. The degree of quaternization was determined by neutralization titration. The intrinsic viscosity was determined with a capillary viscometer of modified Ubbelohde type with four bulbs. The details were reported previously.[12] The molecular characteristics of samples are listed in Table I.

Measurements. Viscosities of relatively high concentrated solutions were measured at room temperature (ca. 25 °C) with fluid spectrometers, types RFS-8500 and RFSII, and a mechanical spectrometer RMS-800 of Rheometrics, Inc. For the fluid spectrometers, we used the cone and plate combination of which the diameter is 5.0 cm long and the cone angle is 0.04 rad and the coaxial cylinder of which the cup radius is 1.7 cm long and the bob radius and length are 1.6 and 3.3 cm long, respectively, and for the mechanical spectrometer, we used the cone and plate combination of which the dimensions are the same as those used for the fluid spectrometers. Strain was applied to the solutions in oscillating and steady-shear flow by the lower plate. For most of the relatively low concentrated solutions, on the other hand, η^0 was measured with capillary viscometers of the Maron–Krieger–Sisko type at 25 °C.[13] To examine the degradation of the samples after the measurements of η^0, we measured $[\eta]$ and confirmed

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Table I
Molecular Characteristics of Poly(*N*-methyl-2-vinylpyridinium chloride)s

sample code	$M_w \times 10^{-5}$	M_w/M_n	DQ,[a] %
MVPK11	6.94	1.07	87.3
MVPK12	11.0	1.09	85.3
MVPK13	27.4	1.13	81.8

[a] DQ represents the degree of quaternization.

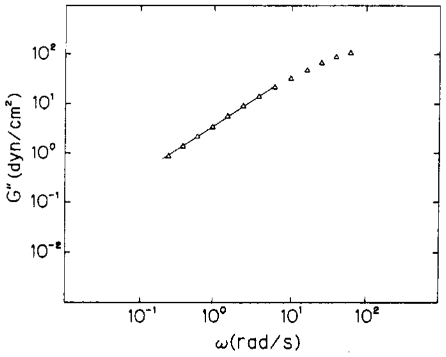

Figure 1. Example of the dependence of G'' on ω. The sample is MVPK-13, C = 0.01 g/cm³ and C_s = 0.01 M.

that there was no degradation. The added salt used was NaCl, and its concentrations C_s were 0.5, 0.1, and 0.01 M.

Polymer solutions in the presence of added salt were prepared by dialyzing the solutions against the aqueous solution with the respective NaCl concentrations to attain Donnan equilibrium in all polymer concentrations measured. Dialysis was carried out by using cellulose tubes at low polymer concentrations and dialysis cells with cellulose membranes at high polymer concentrations. The polymer concentrations (g/cm³) were determined by measuring the UV absorption of solutions at 267 nm as reported previously.[12]

Results

An example of a double-logarithmic plot of loss modulus G'' vs frequency ω for the polyelectrolyte solution is shown in Figure 1. As G'' is proportional to ω in the low-frequency region, i.e., in the terminal region, we evaluated η^0 from the following relationship:

$$\eta^0 = \lim_{\omega \to 0} G''/\omega \qquad (4)$$

Moreover, η^0 was also evaluated from the Newtonian region in steady flow experiments, and we confirmed that both η^0 values agree with each other.

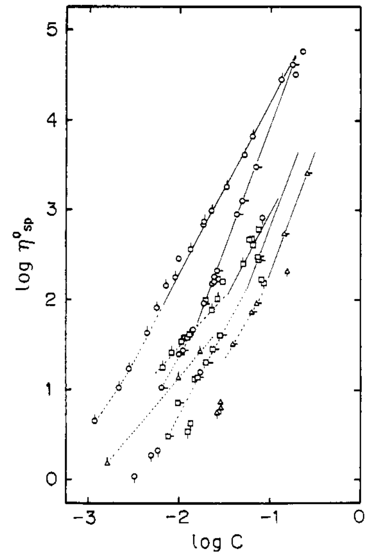

Figure 2. Polymer concentration dependences of η^0_{sp} at various concentrations of added salt. The triangles, squares, and circles denote the data for MVPK-11, MVPK-12, and MVPK-13, respectively. The upward, rightward, and downward pips indicate the data in 0.01, 0.1, and 0.5 M NaCl solutions, respectively. Symbols without pips denote the data in the absence of added salt. The dotted and solid lines were drawn to smoothly connect the data in dilute and semidilute regions, respectively.

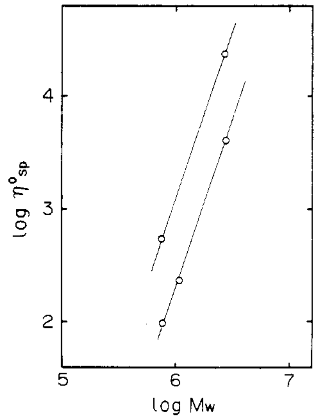

Figure 3. Molecular weight dependence of η^0_{sp} in 0.1 M NaCl solutions. The upper and lower lines denote the data at 0.15 and 0.06 g/cm³, respectively.

Figure 2 shows double-logarithmic plots of η^0_{sp} vs C in 0.5, 0.1, and 0.01 M NaCl solutions and salt-free solutions. η^0_{sp} is larger at lower concentrations of added salt for the same molecular weight, while the polymer concentration dependence is larger at higher concentrations of added salt. A similar dependence of η^0 on the concentration of added salt was reported for poly(sodium acrylate) solutions.[9] In the region where polymer concentrations are high enough, the polymer concentration dependence of η^0_{sp} becomes the same at the same salt concentration, regardless of the molecular weights, as shown by the solid lines. Figure 3 shows double-logarithmic plots of η^0_{sp} vs M_w in 0.1 M NaCl solutions at C = 0.06 and 0.15 g/cm³ where the molecular weight dependence of η^0_{sp} is independent of polymer concentration. This figure reveals that the molecular weight dependence of η^0_{sp} in 0.1 M NaCl solution is given by $\eta^0_{sp} \propto M^3$ denoted by the solid lines. Figures 4–6 show double-logarithmic plots of η^0_{sp}/M^3 vs C in 0.01, 0.1, and 0.5 M NaCl solutions and salt-free solutions, respectively. In each solution, the data at the high polymer concentration region which we call the semidilute region are almost independent of molecular weight and they are approximately given by eq 5.

$$\eta^0_{sp} \propto M^3C^{1.5} \qquad (C_s = 0\ \mathrm{M}) \qquad (5a)$$

$$\eta^0_{sp} \propto M^3C^{1.8} \qquad (C_s = 0.01\ \mathrm{M}) \qquad (5b)$$

$$\eta^0_{sp} \propto M^3C^{2.8} \qquad (C_s = 0.1\ \mathrm{M}) \qquad (5c)$$

$$\eta^0_{sp} \propto M^3C^{4.6} \qquad (C_s = 0.5\ \mathrm{M}) \qquad (5d)$$

In the following discussion, therefore, we assume that η^0_{sp} is proportional to M^3 in the semidilute regions measured here.

In Figures 7–9, the data in the presence of added salt in Figure 2 are replotted in the double-logarithmic form of η^0_R vs $C[\eta]$. As shown in Figures 7 and 8, η^0_R appears to be expressed as a universal function of $C[\eta]$ in 0.5 and 0.1 M NaCl solutions, whereas, apparently, η^0_R is not expressed as a universal function of $C[\eta]$ in 0.01 M NaCl solution as shown in Figure 9.

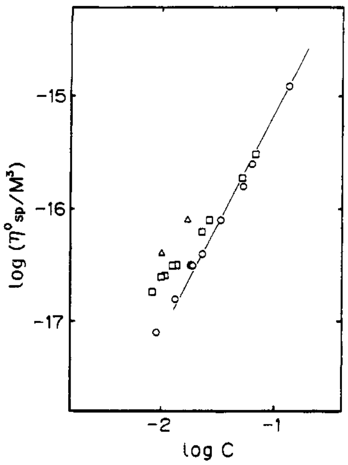

Figure 4. Double-logarithmic plots of η^0_{sp}/M^3 vs C in 0.01 M NaCl solutions. The triangles, squares, and circles denote the data for MVPK-11, MVPK-12, and MVPK-13, respectively. The solid line denotes eq 5b.

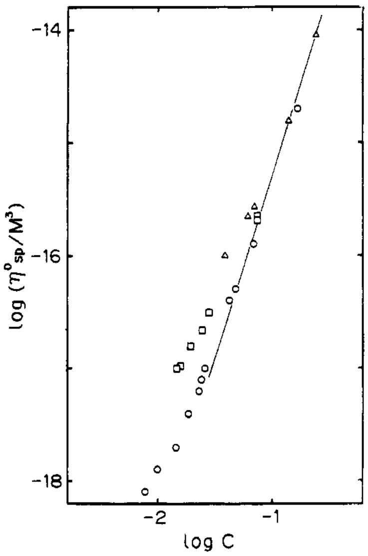

Figure 5. Double-logarithmic plots of η^0_{sp}/M^3 vs C in 0.1 M NaCl solutions. Symbols are the same as in Figure 4. The solid line denotes eq 5c.

To compare the data in semidilute regions with the scaling law, we need the ν values in the NaCl solutions. Thus, we evaluated the ν values assuming $\nu = (a + 1)/3$ from the exponent a in the Mark–Houwink–Sakurada equation, $[\eta] = KM^a$. The equations for PMVP-Cl in the three NaCl solutions are given by[12]

$$[\eta] = 7.86 \times 10^{-5} M_w^{0.86} \quad (C_s = 0.01\ \mathrm{M}) \tag{6a}$$

$$[\eta] = 8.40 \times 10^{-5} M_w^{0.77} \quad (C_s = 0.1\ \mathrm{M}) \tag{6b}$$

$$[\eta] = 26.8 \times 10^{-5} M_w^{0.63} \quad (C_s = 0.5\ \mathrm{M}) \tag{6c}$$

If we assume that $\eta^0_{sp} \propto M^3$ in semidilute regions, eq 3 can be rewritten as

$$\eta^0_R \propto (C/C^*)^{(4-3\nu)/(3\nu-1)} \tag{7a}$$

$$\eta^0_R \propto (C[\eta])^{(4-3\nu)/(3\nu-1)} \tag{7b}$$

Introducing the ν values evaluated from the exponents in eq 6 into eq 7, we have the calculated lines as shown by solid ones in Figures 7–9. In 0.5 M NaCl solutions, the experimental dependence appears to agree with the calculated line, whereas the experimental slopes are lower than the calculated ones in 0.1 and 0.01 M NaCl solutions.

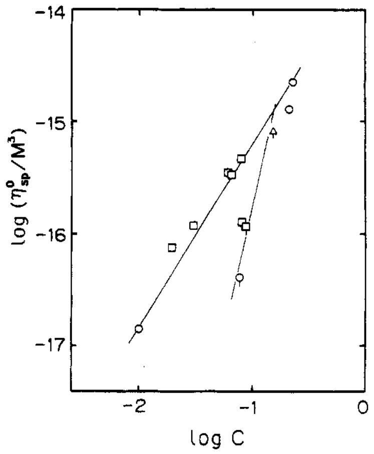

Figure 6. Double-logarithmic plots of η^0_{sp}/M^3 vs C in 0.5 M NaCl and salt-free solutions. Symbols are the same as in Figure 4. The symbols with downward pips and without pips denote the data in 0.5 M NaCl solutions and in the absence of added salt, respectively. The upper and lower solid lines denote eqs 5a and 5d, respectively.

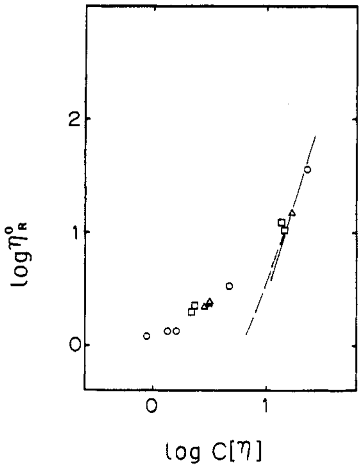

Figure 7. Double-logarithmic plots of η^0_R vs $C[\eta]$ in 0.5 M NaCl solutions. Symbols are the same as in Figure 4. The solid and broken lines denote the values calculated by eqs 7 and 29 in 0.5 M NaCl solution, respectively.

Discussion

Let us discuss the dependence of η^0 on polymer concentration in various concentrations of added salt. Approximately, η^0 in the entangled region is given by the product of the longest relaxation time τ and elastic modulus G.[1,14]

$$\eta^0 \propto \tau G \tag{8}$$

According to the reptation model for polymer melts, τ and G in the entangled region can be given by[1,14]

$$G \propto ck_BT/n \tag{9}$$

$$\tau \propto \zeta_0 NL^2/k_BT \tag{10}$$

where c is the number of segments per unit volume, L is the contour length of a tube, N is the number of segments per polymer chain, n is the number of segments between entanglement points, ζ_0 is the frictional coefficient of the segment, k_B is the Boltzmann constant, and T is the absolute temperature.

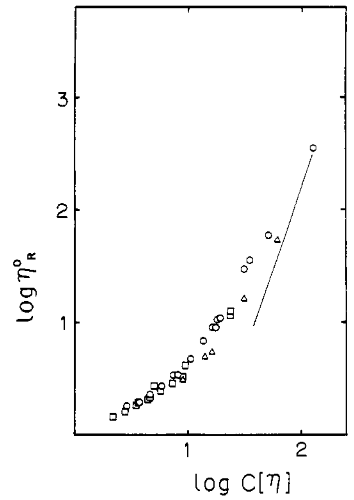

Figure 8. Double-logarithmic plots of η^0_R vs $C[\eta]$ in 0.1 M NaCl solutions. Symbols are the same as in Figure 4. The solid line denotes the value calculated by eq 7 in 0.1 M NaCl solution.

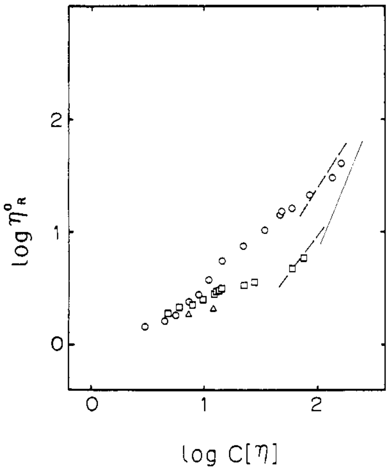

Figure 9. Double-logarithmic plots of η^0_R vs $C[\eta]$ in 0.01 M NaCl solutions. Symbols are the same as in Figure 4. The solid and broken lines denote the values calculated by eqs 7 and 29 in 0.01 M NaCl solution, respectively.

To apply the reptation model to the semidilute regions, we should take into account the hydrodynamic interactions among the segments in the chain between entanglement points.[15] Therefore, the frictional coefficient of a polymer chain in a tube $\zeta_0 N$ in eq 10 should be replaced by the product of the frictional coefficient of chains between entanglement points ζ and the number of chains divided by entanglement points per polymer chain (N/n). Since ζ is assumed to be proportional to $\eta_s a$ according to the nondraining model, and $L = a(N/n)$, where a is the dimension of the chain divided by the entanglement points, eq 10 can be rewritten as

$$\tau \propto (\eta_s/k_BT)(Na/n)^3 \qquad (11)$$

Using eqs 8, 9, and 11, we have

$$\eta^0 \propto \eta_s(N/n)^3a^3c/n \propto \eta_s(N/n)^3 \qquad (12)$$

where the following relationship was used.

$$n \propto ca^3 \qquad (13)$$

Moreover, if we assume that a is proportional to the thermodynamic correlation length ξ and the chain between entanglement points is expanded as a single polyion chain in dilute solutions by an expansion factor α, we have

$$a \propto \xi \sim bn^{1/2}\alpha \qquad (14)$$

and

$$n \propto c\xi^3 \qquad (15)$$

where b is the segment length.

According to Flory,[16] the expansion factor of polyelectrolyte α is determined by minimizing the free energy ΔF, which consists of the mixing free energy of a polyion, solvent molecules, and mobile ions ΔF_M and the elastic free energy ΔF_{el} as

$$\partial\Delta F/\partial\alpha = (\partial\Delta F_M/\partial n_1)(\partial n_1/\partial\alpha) + \partial\Delta F_{el}/\partial\alpha = 0 \qquad (16)$$

where n_1 is the number of solvent molecules.

If we simply assume that the segments in the polyion chain between entanglement points are distributed uniformly in a spherical domain, of which the radius is equal to $R_{g0}\alpha$, n_1 is given by

$$n_1 = (4\pi/3)(R_{g0}^3\alpha^3N_A/v_1) - nvN_A/v_1 \qquad (17)$$

where R_{g0} is the unperturbed radius of gyration of the polyion chain between entanglement points, v is the volume of the segment, and v_1 is the molar volume of the solvent. Differentiating eq 17 with α, we have

$$\partial n_1/\partial\alpha = 4\pi R_{g0}^3N_A\alpha^2/v_1 \qquad (18)$$

In this model, $\partial\Delta F_M/\partial n_1$ is related to the osmotic pressure Π set up between the inside and the outside of a polyion domain. If we assume that the added salt is monovalent and Π is given by the difference of concentrations of mobile ions between the inside and the outside of a polyion domain neglecting the contribution of polyion, we have

$$\partial\Delta F_M/\partial n_1 = -RTv_1(ic + 2C_s - 2C_s^*) \qquad (19)$$

where i is the effective charge of charged segments, in other words, ic is the concentration of mobile counterions from polyelectrolytes, and C_s and C_s^* are the concentrations of added salt inside and outside the polyion domain, respectively.

Assuming the ideal Donnan equilibrium, we have

$$C_s(ic + C_s) = C_s^{*2} \qquad (20)$$

Introducing the solution of eq 20 into eq 19, we have

$$\partial\Delta F_M/\partial n_1 = -RTv_1[(i^2c^2 + 4C_s^{*2})^{1/2} - 2C_s^*] \qquad (21)$$

If we assume that the chain is Gaussian, the elastic free energy ΔF_{el} is given by

$$\Delta F_{el} = k_BT[3(\alpha^2 - 1)/2 - \ln\alpha^3] \qquad (22)$$

Differentiating eq 22 with α, we have

$$\partial\Delta F_{el}/\partial\alpha = 3k_BT(\alpha - 1/\alpha) \qquad (23)$$

Introducing eqs 18, 21, and 23 into eq 16, we have

$$\alpha - 1/\alpha = K_1n^{3/2}\alpha^2[(i^2c^2 + 4C_s^{*2})^{1/2} - 2C_s^*] \qquad (24)$$

where $K_1 = (4\pi/3)b^3N_A^2$. Since we assumed that the segments are uniformly distributed in a spherical domain of chain, c is given by

$$c = n/[(4\pi/3)R_{g0}^3\alpha^3] = K_2/(n^{1/2}\alpha^3) \qquad (25)$$

where $K_2 = (3^{5/2}/2^{1/2}\pi)/b^3$. Introducing eq 25 into eq 24, we have

$$\alpha - 1/\alpha = K_1n^{3/2}\alpha^2[(K_2^2i^2/(n\alpha^6) + 4C_s^{*2})^{1/2} - 2C_s^*] \qquad (26)$$

In the limit of high concentration of added salt, i.e., $C_s^* \gg ic$, we recover the equation of Flory for the expansion

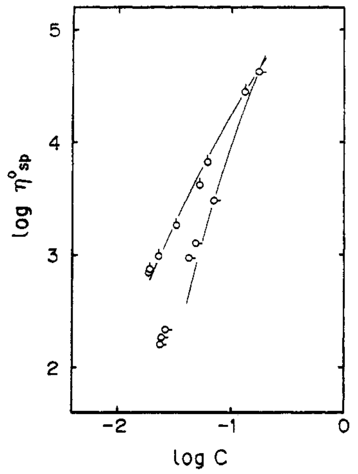

Figure 10. Comparison between observed and calculated dependences of η^0 on C for MVPK-13 in 0.01 and 0.1 M NaCl solutions. Symbols are the same as in Figure 2. Solid lines denote eq 29 shifted along the vertical axis.

of polyelectrolyte having n segments in the presence of added salt.

$$\alpha^5 - \alpha^3 = (K_1K_2^2/2)i^2n^{1/2}/4C_s^* \qquad (27)$$

To make the discussion simpler, we assume that $\alpha \gg 1$, which usually holds for polyelectrolytes, so that we have the following approximate expression for α from eq 24.

$$\alpha^{-1} = K_1n^{3/2}[(i^2c^2 + 4C_s^{*2})^{1/2} - 2C_s^*] \qquad (28)$$

Substituting eqs 14, 15, and 28 into eq 12, we have the following equation for the polymer concentration dependence of η^0 as a function of C_s^*.

$$\eta^0 \sim N^3[(i^2c^2 + 4C_s^{*2})^{1/2} - 2C_s^*]^{9/4}/c^{3/4} \qquad (29)$$

Using eq 27 and the Flory–Fox equation, we have the scaling equation at the high concentration of added salt.

$$\eta^0_{\mathrm{R}} \propto (C/C^*)^{11/4} \propto (C[\eta])^{11/4} \qquad (30)$$

This equation corresponds to eq 7 with $\nu = 0.6$. In salt-free solutions, on the other hand, eq 29 is expressed as

$$\eta^0 \propto N^3c^{1.5} \qquad (31)$$

The theory well explains the experimental results that the polymer concentration dependence of η^0 increases with an increase in the concentration of added salt, as shown by eq 5. As shown in Figure 6 or eq 5a, the data in salt-free solution are in good agreement with eq 31. Figure 10 shows the comparison between observed and calculated dependences of η^0_{sp} on C in different concentrations of added salt. Here, we assumed the effective charge $i = 0.2$[17] and shifted the calculated line along the vertical axis to fit the data in the respective concentration of added salt. This figure reveals that the observed polymer concentration dependences can be well expressed by eq 29 at the respective concentrations of added salt. Moreover, η^0_{R} at high (0.5 M) and low (0.01 M) concentrations of added salt, calculated by eq 29, are shown in Figures 7 and 9, respectively. As shown in Figure 7, the data at high concentration of added salt appear to be explained by the scaling law. At low concentration of added salt, however, the data do not follow the scaling law because the concentration of counterions from the polyelectrolyte increases with an increase in the polymer concentration.

From the above results, we conclude that η^0 in semidilute regions of polyelectrolyte solutions can be explained by the reptation model assuming that the correlation length related to entanglements is determined by the electrostatic interaction evaluated from Donnan equilibrium in the respective concentration of added salt.

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References and Notes

(1) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979; Chapter 3.
(2) Noda, I. In *Molecular Conformation and Dynamics of Macromolecules in Condensed System*; Nagasawa, M., Ed.; Elsevier: Tokyo, 1988.
(3) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 587.
(4) Takahashi, Y.; Isono, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1985**, *18*, 1002.
(5) Takahashi, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1985**, *18*, 2220.
(6) Noda, I.; Tsuge, T.; Nagasawa, M. *J. Phys. Chem.* **1970**, *74*, 710.
(7) Okamoto, H.; Nakajima, H.; Wada, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1035.
(8) Rosser, R. W.; Nemoto, N.; Schrag, J. L.; Ferry, J. D. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1031.
(9) Sakai, M.; Noda, I.; Nagasawa, M. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 1047.
(10) Rinaudo, M.; Graebling, D. *Polym. Bull.* **1986**, *15*, 253.
(11) Morris, E. R.; Rees, D. A.; Welsh, E. J. *J. Mol. Biol.* **1980**, *138*, 383.
(12) Yamaguchi, M.; Yamaguchi, Y.; Matsushita, Y.; Noda, I. *Polym. J. (Tokyo)* **1990**, *22*, 1077.
(13) Maron, S. H.; Krieger, I. M.; Sisko, A. W. *J. Appl. Phys.* **1954**, *25*, 971.
(14) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986; Chapter 7.
(15) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 594.
(16) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter 14.
(17) Nagasawa, M. In *Polyelectrolytes*; Selegny, E., Eds.; D. Reidel Publishing Co.: Boston, MA, 1974.