Macromolecules **1984**, *17*, 1731-1735

Dynamic Light Scattering of Poly(L-lysine) Hydrobromide in Aqueous Solutions

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Received October 12, 1983

ABSTRACT: A dynamic light scattering study has been made on aqueous solutions of a poly(L-lysine) hydrobromide (PLL-HBr) (degree of polymerization 406) at low concentrations of polymer (C_p = 0.04–20 mg cm^{-3}) and of added NaBr salt (C_s = 6.9 × 10^{-5} to 0.302 mol dm^{-3}). The autocorrelation function of the scattered light intensity was of the single-exponential form for all solutions tested but special ones whose composition obeys C_p^* = (constant) × $C_s^{*-0.53}$. The dependence of the diffusion coefficient on C_p and C_s was quantitatively reproduced by the existing theory of the charge effect over a fairly wide range of the variables. The polymer chains assume a considerably extended form at extremely low values of C_p and C_s. It has been conjectured that an ordered cluster of a number of PLL-HBr molecules is formed by the delicate balance between the charge effect and the conformational effect, and the internal motion of the cluster becomes observable over a very restricted range of concentrations.

Introduction

Poly(L-lysine) hydrohalides are highly charged macromolecules whose diffusion behavior is still controversial. Daniel and Alexandrowicz[1] performed diffusion measurements in a low-speed ultracentrifuge over a wide range of polymer and added salt concentrations, C_p and C_s, and found that, for example, the apparent diffusion coefficient D of a poly(L-lysine) hydrochloride (PLL-HCl) with polymerization degree n = 340 increased from 2.5 × 10^{-7} in an excess-of-salt solution to 50 × 10^{-7} cm^2 s^{-1} in a salt-free solution. The remarkable increase in D can be attributed to the dragging effect exerted by the small ions.[2] They did not observe any indication of the formation of ordered phase in the tested range $C_s > 0.01$ M and $C_s = 0$.

On the contrary, Schurr, Lee, and Lin[3,4] observed in a series of dynamic light scattering (DLS) studies on a poly(L-lysine) hydrobromide (PLL-HBr, n = 955) that the autocorrelation function $A(\tau)$ of solutions with C_p = 1 mg cm^{-3} exhibited non-single-exponential behavior over a very narrow range of C_s between 0.0009 and 0.0010 M and that D became as small as 0.1 × 10^{-7} cm^2 s^{-1} on the low-C_s side of this narrow range. They regarded this complicated change in D as evidence of formation of a new phase, the extraordinary phase in their terms. They were, however, not able to detect experimentally the enhanced diffusion coefficient in salt-free solutions.

In connection with this subject, it may be pertinent to refer to the two-state structure model of macroion solutions presented by Ise and Okubo.[5,6] They have recently performed small-angle X-ray scattering (SAXS) measurements on various highly charged macromolecules, including PLL-HBr,[7] and found that a distinct peak appears in each SAXS curve obtained in salt-free or low-C_s solutions. The nearest macroion distance estimated from the SAXS peak position by using the Bragg equation was always smaller by a factor 2 or more than the value obtained by assuming an ordered lattice extending over the entire solution. Ise and Okubo have counted this as evidence for the two-state structure of the solutions, in which an ordered region having a shorter intermacroion distance coexists with the remaining disordered region having a longer average distance. However, it may not necessarily be justified to identify the extraordinary phase of Schurr et al. with the ordered phase of Ise et al., because the range of PLL-HBr concentration C_p surveyed by DLS was 1–3 mg cm^{-3} whereas that by SAXS was 20–40 mg cm^{-3}.

In view of the above-mentioned situation, problems remain unsettled concerning the diffusion behavior of PLL-HBr in low-salt solutions. The present DLS study has been performed to obtain a more clear understanding of those problems.

Experimental Section

Materials. Poly(L-lysine) hydrobromide (PLL-HBr) used in this study was the same sample (Miles, lot no. 202) used by Ise et al. in their SAXS study.[7] The degree of polymerization n was 406 (or weight-average molecular weight 84 800). The sample was dialyzed against carefully purified water by using a cellotube. The dialysis was conducted in a nitrogen box for 4 days and the sample was freeze-dried.

Water used for solution preparation was purified by ion exchange and subsequent distillation under a nitrogen atmosphere from a quartz vessel. The specific conductance of this water was 3.0 × 10^{-7} Ω^{-1} cm^{-1}, which was measured by a Wayne-Kerr autobalance precision conductance bridge B311. The atomic absorption spectra of the water and PLL-HBr indicated that amounts of cations such as Na$^+$ and K$^+$ were negligibly small. NaBr used was of a guaranteed grade from Nakarai Chemicals, Ltd., Kyoto.

The freeze-dried polymer was dissolved in filtered water containing known amounts of NaBr. Each solution was filtered in a dust-free box by a Millipore filter (nominal pore size, 0.1 μm) and poured directly into a dust-free light scattering cell. A series of solutions with different polymer concentrations C_p were prepared at each salt concentration of C_s = 6.92 × 10^{-5}, 7.41 × 10^{-4}, 2.00 × 10^{-3}, 5.75 × 10^{-3}, 7.41 × 10^{-2}, and 3.02 × 10^{-1} mol dm^{-3}, and they were used for DLS measurements. The C_p ranged from 0.04 to 20 mg cm^{-3}. The highest C_p was chosen so as to meet the lowest C_p chosen in the SAXS study of Ise's group.

Circular dichroism (CD) measurements were made on nine solutions arbitrarily selected. All spectra exhibited a positive maximum at around 217 nm, which is characteristic of the random conformation of PLL-HBr. The peak height, which is a sensitive measure of C_p, was not affected by filtration.

Method. The DLS instrument used has been described earlier.[8] A single-frequency 488-nm line of an argon ion laser (Spectra Physics, Model 165-03) with an output power of 300 mW was used as a light source. The vertical component of the scattered light from a solution in a sample cell (NMR tube with outer diameter of 12 mm) was detected by photomultipliers (Hamamatsu TV) attached at five fixed scattering angle θ, i.e., 30°, 60°, 90°, 120°, and 150°. The homodyne autocorrelation function $A(\tau)$ was measured at 25 ± 0.02 °C by using either a time interval correlator with 512 channels (Union Giken Co., Osaka) or a shift register correlator with 72 channels (Malvern).

Results

Relatively High Salt Concentrations, $C_s > 0.01$ M. At the two highest NaBr concentrations tested, i.e., C_s = 0.302 and 0.0741 mol dm^{-3}, the PLL-HBr solutions scatter

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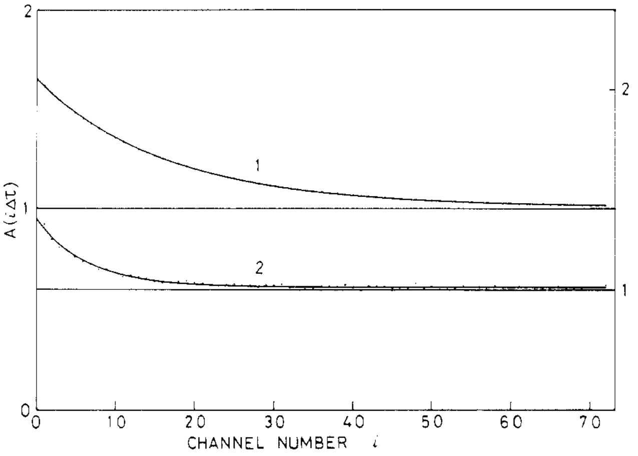

Figure 1. Intensity autocorrelation function $A(i\Delta\tau)$ of aqueous solutions of PLL-HBr at relatively high and low concentrations of NaBr. Channel number i = 1–72 and scattering angle θ = 30°. Upper data (1): C_p = 3 mg cm^{-3}, C_s = 0.302 mol dm^{-3}, $\Delta\tau$ = 15 μs. Lower data (2): C_p = 3 mg cm^{-3}, C_s = 0.002 mol dm^{-3}, $\Delta\tau$ = 4 μs. The solid lines represent the best fit curves of single-exponential form, eq 1. The ordinate for the lower data (2) is shifted downward by 0.40, as shown on the right-hand ordinate in the figure.

Table I
Diffusion Coefficients of PLL-HBr in Dilute Aqueous Solutions with Small Amounts of Added NaBr Salt at 25 °C

C_s, mol dm^{-3}	C_p, mg cm^{-3}	$D \times 10^7$, cm^2 s^{-1}	C_s, mol dm^{-3}	C_p, mg cm^{-3}	$D \times 10^7$, cm^2 s^{-1}
3.02 × 10^{-1}	3.0	2.6	2.00 × 10^{-3}	5.0	32
	2.0	2.4		3.0	26
	1.0	2.2		1.0	11
	0.5	2.0		0.50	3.2
	0.25	2.0		0.25	2.4
7.41 × 10^{-2}	3.0	3.0		0.10	1.8
	1.5	2.4		0.050	1.6
	1.0	2.4	7.41 × 10^{-4}	4.2	40
	0.5	2.2		3.0	30
	0.32	1.9		0.84	10
5.75 × 10^{-3}	5.0	18		0.75	12
	3.0	16		0.42	9.1
	1.0	8.0		0.21	4.4
	0.5	3.3		0.08	1.9
	0.25	2.3	6.92 × 10^{-5}	5.0	40
	0.10	1.7		4.2	39
2.00 × 10^{-3}	20	48		3.0	42
	10	42		1.5	30

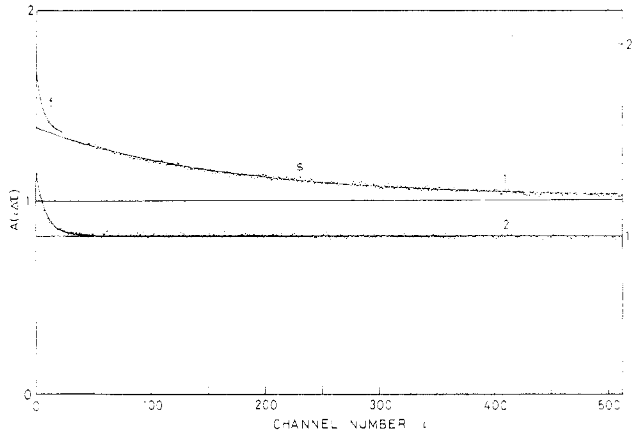

Figure 2. Two types of the intensity correlation functions $A(i\Delta\tau)$ obtained at fixed NaBr concentration C_s = 0.002 mol dm^{-3} but at different polymer concentrations. Upper data (1) of the non-single-exponential type: C_p = 0.5 mg cm^{-3}, $\Delta\tau$ = 40 μs. Lower data (2) of the single-exponential type: C_p = 3.0 mg cm^{-3}, $\Delta\tau$ = 3 μs. The ordinate for the lower data (2) is shifted downward by 0.19, as shown on the right-hand ordinate in the figure.

light with almost the same average intensity $\langle I_s \rangle$ as solutions of neutral polymers, and the intensity autocorrelation function $A(\tau)$ can be measured with very high precision. A typical result of measurement is shown in the upper half of Figure 1, where the data points $A(i\Delta\tau)$ for a solution with C_s = 0.302 mol dm^{-3} and C_p = 3.0 mg cm^{-3} are plotted against the channel number i. The clock pulse interval $\Delta\tau$ was 15 μs and the scattering angle θ was 30°. The data were fitted to a three-parameter equation of single-exponential form

$$A(\tau) = (1 + b) + a \exp(-2\Gamma\tau) \qquad (1)$$

by using the least-squares method. The solid curve 1 in the figure was drawn with b = 0.009, a = 0.645, and Γ = 2026 s^{-1}. Since b is small and the variance (second cumulant) has also been found to be small (0.045), we can expect that the above estimate of decay rate Γ is accurate, say to within 2%.

The Γ thus determined is proportional to the square of the scattering vector, $q^2 = (16\pi^2/\lambda^2) \sin^2 (\theta/2)$, where λ is the wavelength in the medium, and we obtain the diffusion coefficient D of PLL-HBr in two high-salt solutions as shown in Table I.

Low Salt Concentrations: Bimodal Behavior. As already mentioned, Lin et al.[4] have found that $A(\tau)$ of the solutions of a PLL-HBr with n = 955 involves two decay modes when C_p = 1.0 mg cm^{-3} and C_s = (0.9–1.0) × 10^{-3} mol dm^{-3}. We have also observed that the present sample with n = 406 shows $A(\tau)$ of a non-single-exponential form under three conditions of concentration: (A) C_s = 2.00 × 10^{-3} mol dm^{-3} and C_p = 0.50 mg cm^{-3}, (B) C_s = 7.41 × 10^{-4} mol dm^{-3} and C_p = 0.84 mg cm^{-3}, and (C) C_s = 6.92 × 10^{-5} mol dm^{-3} and C_p = 3.0 mg cm^{-3}.

An example of the non-single-exponential $A(\tau)$ is shown in the upper half of Figure 2, which was obtained with $\Delta\tau$ = 40 μs for solution A at θ = 30°. Two curves f and s each represent single-exponential functions of the form of eq 1. The fast decay curve f was obtained by fitting the data points from 1 to 30 channels to eq 1, and the slow one s by fitting the data points from 50 to 511 channels again to eq 1. The decay rates thus determined were Γ_f = 2500 s^{-1} and Γ_s = 65 s^{-1}, and the base line parameter was substantial only for the fast mode, actually b_f = 0.24 and b_s = 0.01, respectively. The same data have also been analyzed by using a four-parameter equation

$$A(\tau) = 1 + \{a_f \exp(-\Gamma_f\tau) + a_s \exp(-\Gamma_s\tau)\}^2 \qquad (2)$$

The decay rates Γ_f and Γ_s thus obtained were in agreement with those obtained by the former approximate method within experimental errors of about 10%, provided that the two rates were different from each other by a factor of 10.

The Γ_f and Γ_s obtained for solutions A and B are plotted against q^2 on a logarithmic scale in Figure 3, where probable errors are indicated by the bars. The Γ_f are proportional to the square of q, whereas the Γ_s are proportional to a high power, 2.75 ± 0.15. The latter index is close to the one that has been reported for the internal motion of a nonionic flexible polymer.[9]

The bimodal relaxation behavior of solution C was recognized by repeating $A(\tau)$ measurements on different time scales, since the two rates Γ_f and Γ_s are too widely separated. Thus, for example at θ = 30°, we obtained Γ_f = 3.7 × 10^4 s^{-1} and b_f = 0.31 by fitting to eq 1 the first 150 points of the total 510 data points measured with $\Delta\tau$ = 0.4 μs and also obtained Γ_s = 25 s^{-1} and b_s = 0.009 by fitting all 72 points measured with $\Delta\tau$ = 700 μs again to eq 1. The Γ_f and Γ_s of solution C are included in Figure 3. Larger

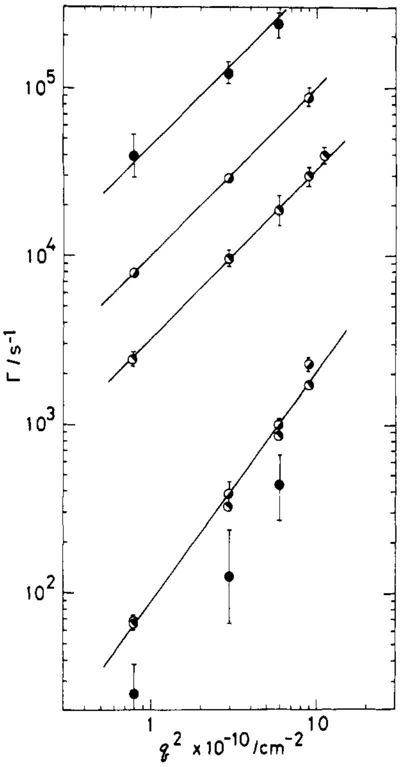

Figure 3. Fast and slow decay rates, Γ_f and Γ_s, plotted against the squared scattering vector, q^2: (◐) solution A; (◑) solution B; (●) solution C.

Table II
Comparison of Average Scattered Intensity of Solutions A and B with That of Related Solutions

C_s, mol dm^{-3}	C_p, mg cm^{-3}	$\langle I_s \rangle$,[a] photon/s scattering angle 30°	60°
2.00×10^{-3}	1.0	1100	1200
	0.5 (A)	3600	6100
	0.25	1100	1600
7.41×10^{-4}	3.0	2000	2100
	0.84 (B)	5000	4100
	0.42	1100	1900

[a] Neither solvent background correction nor angular correction for scattering volume has been made. $\langle I_s \rangle$ of pure water and 30° and 60° are 420 and 660 photon/s, respectively.

errors in Γ as indicated by the bars were unavoidable because of the extremely low intensity of scattered light from this solution.

The average scattered intensity $\langle I_s \rangle$ from solutions A and B is shown in Table II, together with that from solutions with the same C_s but different C_p. $\langle I_s \rangle$ of the former solutions are larger than those of the latter with the same C_s by a factor 2 or 4 at both scattering angles, 30° and 60°. It was also noted during measurements of $A(\tau)$ that the photon count I_s from solutions A and B occasionally reached about $2\langle I_s \rangle$ and that once such a large fluctuation occurred, it persisted for a long time, say 5 s. In the case of solution A, the slow mode became observable at about 2 h after preparation of the solution. In the case of solution B, the function $A(\tau)$ involved only the fast mode at 30 min after preparation of the solution, but it became bimodal after the solution was kept at 6 °C overnight.

Low Salt Concentrations: Unimodal Behavior. Solutions with low C_s mostly gave correlation functions $A(\tau)$ of the single-exponential type. Examples are shown in the lower halves of Figures 1 and 2. In Figure 1, the $A(i\Delta\tau)$ obtained at $\theta = 30°$ for a solution with $C_s = 0.002$ mol dm^{-3} and $C_p = 3$ mg cm^{-3} are plotted against channel number i with $\Delta\tau = 4$ μs, and the values calculated by eq 1 with $\Gamma = 1.94 \times 10^4$ s^{-1} and $b = 0.02$ are shown by the solid curve 2. The unimodal nature of $A(\tau)$ can be confirmed by the small b. This will be seen more clearly in Figure 2, where the observed correlation over an extended range (i = 1–511 and $\Delta\tau$ = 3 μs) is compared with the same calculated curve 2 as that in Figure 1.

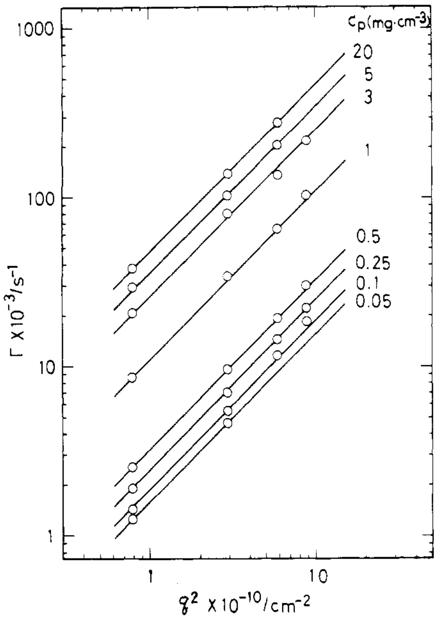

Figure 4. Double-logarithmic plots of Γ against q^2 for a series of solutions at fixed C_s = 0.002 mol dm^{-3}. The number attached to each line represents polymer concentration C_p in mg cm^{-3}.

The Γ's obtained for a series of solutions with the same C_s but different C_p are plotted against q^2 in Figure 4, where the Γ_f data of solution A shown in Figure 3 are once again plotted for the sake of comparison. The Γ of each solution is proportional to q^2, and we can readily determine the apparent diffusion coefficient D within an error of 10%.

A similar treatment of $A(\tau)$ was performed on three other series of solutions with $C_s = 5.75 \times 10^{-3}$, 7.41×10^{-4}, and 6.92×10^{-5} mol dm^{-3}. In the last series, the scattered intensity was so low at $C_p < 1.0$ mg cm^{-3} that reliable values of D were not obtainable. The values of D thus determined are summarized in Table I.

Discussion

Diffusion Coefficient at High C_s and Low C_p. The diffusion behavior of PLL-HBr at high C_s is not our main concern, since the subject has already been studied extensively by Daniel and Alexandrowicz.[1] We simply note that the present data of D obtained at C_s = 0.30 and 0.074 M obey the linear dependence

$$D = D_p[1 + (\beta^2 n^2/2)(C_p/C_s)] \qquad (3)$$

where β is the fraction of free counterions[10] and both C_p and C_s are to be expressed in moles of polymer and added salt per unit volume of solution, respectively. D_p was obtained as 2.00×10^{-7} cm^2 s^{-1} for both C_s = 0.30 M and C_s = 0.074 M, and β was 0.17 and 0.11 for C_s = 0.30 and 0.074 M, respectively. These values of β for the present sample with n = 406 are compared favorably with the values, 0.21, 0.13, and 0.10, obtained by Daniel and Alexandrowicz for three samples of PLL-HCl with n = 50, 340, and 900, respectively.

Charge Effect on D at Low C_s. The Kedem–Katchalsky equation[11] of the apparent diffusion coefficient for macroions in salt-free solutions can be written as

$$1/D = (1/n\beta D_p) + (1/D_s) \qquad (4)$$

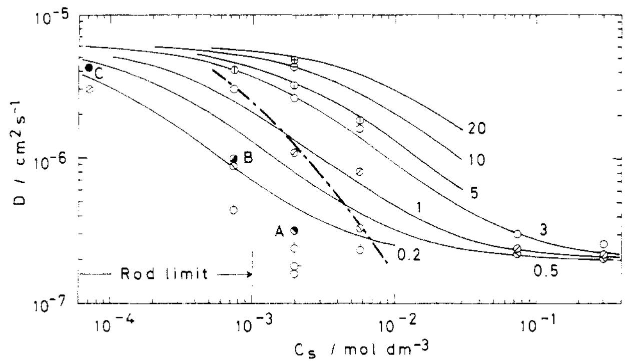

Figure 5. Apparent diffusion coefficient D as a function of C_s and C_p. The solid lines each represent the theoretical dependence of D on C_s at fixed C_p which is calculated by eq 5 and 6. The number attached to each line represents C_p in mg cm^{-3}. C_p (in mg cm^{-3}): (⊕) 20; (⊖) 10; (⦶) 5; (○, ●) 3; (⌀, ◑) 1.5, 1, and 0.84; (⦸, ◐) 0.5 and 0.42; (ό) 0.25 and 0.21; (○) 0.1; (ϙ) 0.05. The dot-dash line represents a boundary where a discrepancy between theory and experiment begins to arise.

where D_s represents the diffusion coefficient of small counterions. Daniel and Alexandrowicz obtained $D = 55 \times 10^{-7}$ and 50×10^{-7} cm^2 s^{-1} for PLL-HCl with $n = 50$ and 340, which were in reasonable agreement with the values calculated by eq 4.[1] We have also obtained enhanced values, $D = (40\text{–}50) \times 10^{-7}$ cm^2 s^{-1}, for PLL-HBr at small values of the ratio of C_s to C_p, as shown in Table I.

Schurr et al.[3,12] have recently presented a theory of the electrically neutral fluctuation of local permittivity in polyelectrolyte solutions and derived a single-exponential autocorrelation function for the scattered light intensity. They have shown that the apparent diffusion coefficient D can be written in the following form over the experimentally accessible range of concentrations and scattering angles:

$$D = \Gamma/q^2 = (1/2)[D_p(1 - \Omega) + D_s(1 + \Omega)] \quad (5)$$

where

$$\Omega = \frac{D_p - (D_s/\beta n)[1 + 2(C_s/\beta n C_p)]}{D_p + (D_s/\beta n)[1 + 2(C_s/\beta n C_p)]} \quad (6)$$

This equation reduces to eq 3 and 4 in the limits $C_p/C_s \ll 1$ and $C_s/C_p \ll 1$, respectively.

The present data are in good agreement with eq 5 as shown in Figure 5, where various types of circles represent the experimental values and the solid curves the values calculated by eq 5. The parameter values adopted were $\beta = 0.12$, $D_p = 2.00 \times 10^{-7}$ cm^2 s^{-1} (observed value), and $D_s = 1.55 \times 10^{-5}$ cm^2 s^{-1} (literature value for NaBr cited in ref 4), respectively. The dot-dash line in Figure 5 indicates a possible location of a boundary where discrepancy between theory and experiment begins to arise.

The discrepancy becomes marked when C_p and C_s both become extremely low. For example, at $C_s = 0.002$ M, the diffusion coefficient D decreased to 1.6×10^{-7} cm^2 s^{-1} with decreasing C_p. This value of D is close to 1.62×10^{-7} cm^2 s^{-1}, the theoretical value for a rod of 1470-Å length and 12-Å diameter, which corresponds to the fully stretched form of our PLL-HBr molecule. These figures suggest that the diffusion behavior in the region of low C_p and low C_s is to be interpreted in terms of the conformational effect as well as the charge effect.

Bimodal Behavior of $A(\tau)$. The concentrations C_s^* and C_p^* where $A(\tau)$ exhibits the bimodal behavior satisfy the simple relationship

$$C_p^* = (\text{constant}) \times C_s^{*-0.53} \quad (7)$$

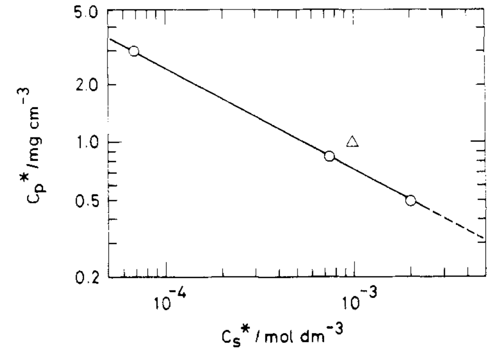

Figure 6. Correlation between C_s^* and C_p^*. Circles represent, from right to left, solutions A, B, and C, and the triangle represents the point found by Lin et al.

though its theoretical meaning is not clarified as yet. The correlation between C_p^* and C_s^* is shown in Figure 6.

The diffusion coefficients specifying the fast decay mode are plotted by filled or half-filled circles in Figure 5. These points appreciably deviate downward from the corresponding curves of eq 5, and the reduction in D may be ascribed partly to the chain stretching and partly to increased interference between molecules.

As already mentioned, the slow decay mode is not the true diffusive mode and disappears outside of the narrow range around C_s^* and C_p^*. The average scattered intensity $\langle I_s \rangle$ is enhanced in the bimodal regime. In addition, we could not detect any large particle by the sedimentation velocity technique, although measurements were performed repeatedly with a change of rotor speed by a factor of 10. On the basis of these observations, we may conclude that an ordered cluster of a number of PLL-HBr molecules is formed in solutions due to a delicate balance between the charge effect and the conformational effect and that the collective internal motion of molecules in the cluster gives rise to the slow decay mode of $A(\tau)$. The cluster seems to be destroyed easily by applying a weak external force. This conjecture is, in many respects, influenced by the two-state structure model proposed by Ise and Okubo.

After this paper was submitted for publication, we became aware of two interesting papers. Wilcoxon and Schurr (*J. Chem. Phys.* **1983**, *78*, 3354) have published results of electrophoretic light scattering and dynamic light scattering measurements on the same polymer samples of n = 406, 946, and 2273 over a wide range of C_s and C_p. They not only have confirmed the transition from the ordinary to the extraordinary phase at low C_s again but have also shown that incorporation of electrolyte friction into Manning's theory could improve the agreement with experimental findings on electrophoretic mobility μ_e. Fulmer, Benbast, and Bloomfield (*Biopolymers* **1981**, *20*, 1147) have reported that autocorrelation functions of DNA exhibited a transition from a single-exponential to a two-exponential type of decay around 10^{-2} M ionic strength. Two D_{app} values in the bimodal region were found to be different by 2 orders in magnitude. They have also shown that the amplitude associated with the slow mode is independent of the ionic strength.

Acknowledgment. We are greatly indebted to Prof. N. Ise for valuable advice and discussions and also for the gift of the sample. We also thank Mr. K. Yamamoto for help in purification of PLL-HBr and water and Prof. N. Imai for valuable discussions on the nature of macroion clustering. This work was supported by Grants-in-Aid for Scientific Research (56550629, 58550591) and a Grant-in-Aid for Cooperative Research (57350051) from the Ministry of Education, Science, and Culuture, Japan.

Registry No. Poly(L-lysine) hydrobromide (homopolymer), 56148-61-9; poly(L-lysine) hydrobromide (SRU), 26588-20-5.

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Soliton Model for Dielectric Relaxation in Crystalline Polyethylene. Comparison with Experiment

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Received December 21, 1983

ABSTRACT: The Brownian soliton model for dielectric relaxation in crystalline polyethylene previously introduced by Skinner and Wolynes is used to analyze recent constant-volume experiments by Sayre et al. The non-Debye frequency dependence of the experimental susceptibility is fit extremely well by the theory. From our analysis we determine the temperature dependence of the soliton density. This leads to a value of the soliton energy that is in excellent agreement with an independent theoretical calculation. We speculate about the nature of soliton scattering in this system.

1. Introduction

Dielectric relaxation is a powerful method for probing molecular motion in condensed phases. In this paper we will be concerned with the orientational dynamics of polymer subunits in crystalline polyethylene. (Polyethylene is rendered dielectrically active by dilute oxidation.[1]) Since molecular reorientation is thermally activated, it is desirable to perform experiments at different temperatures. However, in general the volume of the sample is temperature dependent, and activation barriers are sensitive functions of volume. This entanglement of temperature and density effects complicates the analysis of experimental data. Recently, however, with the use of high-pressure techniques, a beautiful set of *constant-volume* experiments[1] have been performed that circumvent the above-mentioned problem.

The experiments on crystalline polyethylene show several relaxation processes, the slowest of which is known as the α-relaxation. This relaxation peak has been analyzed by fitting the frequency-dependent susceptibility to the empirical Cole–Cole equation,[2] finding, for example, that the width parameter is quite temperature dependent. In addition, the temperature dependence of the frequency of maximum loss is analyzed with absolute rate theory, giving the free energy of activation. While these approaches are useful in quantifying experimental data, they do not provide an unambiguous molecular mechanism for the relaxation process.

Although various molecular mechanisms for the α-relaxation process have been proposed (see the excellent discussion in ref 3), the most likely candidate was identified by Mansfield and Boyd.[3] They studied the energetics of defects in crystalline polyethylene with a potential energy surface discussed earlier by Boyd.[4] In particular, they discovered a mobile, localized defect with a creation energy of 18 kcal/mol. The defect is a 180° twist of an all-trans chain localized over about 12 CH_2 units. They found that about half of the creation energy resulted from the twisted region, while the other half stemmed from the translational mismatch of the chain ends. Furthermore, they found that the energy barrier to propagation of the twist was negligible, resulting in its high mobility. The passage of one of these mobile defects past a site with a dipole would cause dielectric relaxation by producing a 180° flip of the dipole.

Independently, Mansfield[5] and Skinner and Wolynes[6] recognized that this defect had the properties of a solitary wave and might well be modeled by soliton theory.[7] Mansfield[5] constructed a model with a rotational and translational degree of freedom for each CH_2 unit and concluded that the resulting equations of motion had solitary wave solutions. Skinner and Wolynes[6] (SW) considered only rotational degrees of freedom and described the system with the familiar sine–Gordon theory. While the latter approach is cruder than Mansfield's (because SW neglected translational degrees of freedom), it is in some ways more attractive because of its analytical tractability.

The frequency-dependent susceptibility is related through linear response theory to the dipole–dipole correlation function.[8] SW calculated the soliton contribution to this correlation function, finding exponential decay. This produces a Debye semicircle in the Cole–Cole plot, in disagreement with experiment. Thus, SW were prompted to consider the interactions of solitons with intrachain phonons or a thermal bath. On the basis of work of others,[9-11] SW proposed that the solutions undergo Brownian motion and calculated the resulting correlation function.

The purpose of this paper is to perform a detailed comparison of experiment[1] with the theory of SW. In section 2, we describe the theory of SW in some detail. In section 3, we fit the frequency-dependent data[1] for different temperatures, and we analyze the temperature dependence of the resulting parameters. We also speculate about the nature of soliton scattering in this system.

2. Soliton Model

From molecular mechanics modeling, Mansfield and Boyd[3] (MB) discovered the existence of a new kind of

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