Anisotropic Translational Diffusion in Dilute Aqueous Solutions of Partially Hydrolyzed Polyacrylamide by Quasielastic Light Scattering

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ABSTRACT: Studies of the Rayleigh spectra of dilute aqueous solutions of partially hydrolyzed polyacrylamide by optical mixing spectroscopy indicate two quite different modes of translational diffusion of the macromolecules which merge on increasing the ionic strength of the solution. These observations can be explained by a model in which, at low ionic strength, frequent intermolecular encounters of the highly extended, rodlike molecules results in highly hindered rotational diffusion so that the molecules have only a librational degree of freedom. Consequently there are two distinct modes of partially rotation-averaged translational diffusion, one parallel to the molecular axis, and one perpendicular to the axis. On increasing the ionic strength, collapse of the extended conformation occurs causing the two modes of motion to merge.

In the limit of very dilute solutions where intermolecular interactions are negligible, the technique of quasielastic light scattering has been established[2a,b] as a useful means of obtaining the translational diffusion coefficients of macromolecular species. At lower scattering vectors $\bar{\kappa}$, the rotationally averaged value for the diffusion coefficient is obtained $\langle D_t \rangle_\phi$ and the quasielastic spectrum is a Lorentzian with halfwidth $2\langle D_t \rangle_\phi \kappa^2$, if the macromolecular species is not widely polydisperse. At larger vectors, however, when $\kappa \cdot l \geq 1$ for nonspherically symmetric molecules of length l, a more complex situation obtains and in general the spectrum is not Lorentzian but has a line width with a more complicated dependence on the anisotropic diffusion coefficients $D_\parallel$ and $D_\perp$ and the rotational diffusion coefficient D_r.[3,4]

The gel state which is the opposite extreme to the case of the noninteracting dilute solution, has recently been studied by Prins *et al.*[5] who observed quasielastic light scattering from collective oscillatory modes in microheterogeneities of the gel. This note reports a preliminary investigation of the macromolecular dynamics in dilute aqueous solutions of a commercially available, high molecular weight, partially hydrolyzed polyacrylamide (The sample used in this study is manufactured by the Dow Chemical Company and is marketed as Pusher 700 polymer.) We believe these solutions represent a fluid state intermediate between that of the noninteracting dilute solution and the network gel. The polyacrylamide molecules are apparently in a highly extended configuration with a conformational shape resembling a long rod rather than a sphere, as is customary for flexible polyelectrolytes of this type.[6] The frequent intermolecular encounters of the highly extended polyacrylamide molecules destroy much of the diffusional freedom of the macromolecules; the strong, intermolecular interactions of the highly polar molecules result in a preferred average orientation between the macromolecular species during collisions; rotational averaging of translational diffusion is no longer possible, since the polymer chains have only a librational degree of freedom; and two distinct translational diffusion modes are observed.

The first, narrow component in the frequency spectrum represents a slow motion which corresponds to partially rotation-averaged diffusion perpendicular to the macromolecular chain axis and is described by the "transverse" diffusion coefficient $\langle D_\perp \rangle_\phi$. The second, broad component corresponding to a faster "longitudinal" motion represents diffusion parallel to the chain axis and is described by the "longitudinal" diffusion coefficient $\langle D_\parallel \rangle_\phi$. These two external diffusion modes are apparently well-defined in the sense that by varying the scattering angle one can observe the κ^2 dependence characteristic of diffusion scattering for both modes. At some intermediate scattering angle, in our system at $\theta = 30°$, the spectrum can be approximately resolved as a superposition of both modes, but at smaller angles will have a more complicated analytical form.

Samples of the partially hydrolyzed polyacrylamide which has a viscosity molecular weight of the order 10^6 and is hydrolyzed to the extent of 19.5% were prepared by dilution with distilled deionized water (equivalent to less than 0.02 ppm of NaCl) to 0.025% by weight. The pH of the solution was 9.28. These samples were then ultracentrifuged at 29,000 rpm for 2 hr to remove macroscopic debris and hence improve the low-frequency resolution of the quasielastic spectra. The use of centrifugation to remove debris undoubtedly reduced the initial concentration of the polymer. The ultracentrifuged samples were then examined with the beat-frequency spectrometer in the heterodyne mode. In this mode a ground-glass thermocouple jacket is partially inserted in the laser beam to provide elastic scattering which acts as a local oscillator. The characteristics of our heterodyne spectrometer particularly with respect to flat frequency response have been thoroughly described elsewhere.[7]

The square-root power spectra at scattering angles θ = 10, 30, 60, and 90° and temperature 19.5° were recorded on a Tektronix 1L5 spectrum analyzer and averaged by 200 20-sec scans across the memory of a Digital Equipment Corp. LAB-8 computer package. The DEC computer was also used to fit Lorentzians to the experimental data using the Lorcap program from the DEC library. Figure 1 shows the angular variation of the halfwidth of the square-root isotropic spectrum. The line width $\Delta\nu_{1/2}{}^{\mathrm{sq\ rt}}$ at large angles apparently has, to a good approximation, the quadratic dependence on sin $\theta/2$ characteristic of

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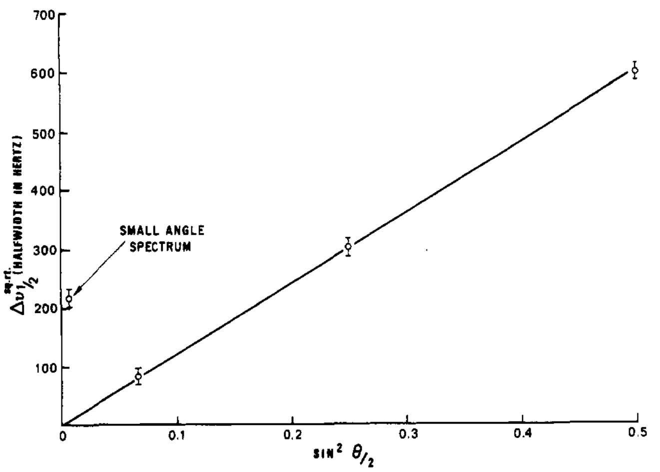

Figure 1. Angular dependence of the halfwidth of the square-root power spectrum of a 0.025% solution of Pusher-700* in deionized water at 19.5°. The small-angle spectrum is clearly the result of scattering from a molecular relaxation process quite distinct from the translational diffusion mode which gives rise to the wide-angle spectra

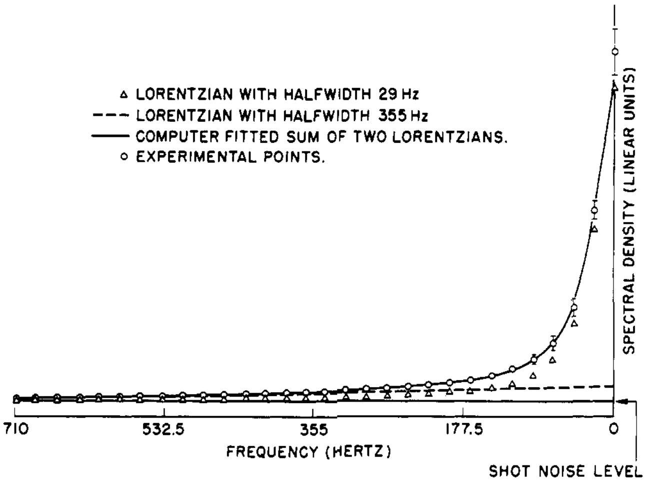

Figure 2. Two-Lorentzian computer fit to the squared spectrum of 0.025% solution of Pusher-700* in deionized water at 19.5°, the ratio of the halfwidths, of the two components (0.08:1) is within experimental error indistinguishable from that of the two diffusion coefficients (0.05:1) of the transverse and longitudinal modes.

Doppler broadening by "pure" translational diffusion[2]

$$\Delta\nu_{1/2}^{\text{sq rt}} = \frac{\sqrt{3}}{\pi}\langle D_t\rangle_{\phi}\kappa^2 \qquad (1)$$

Here D_t is the translational diffusion coefficient of the polymer and $|\kappa| = (4n\pi/\lambda)\sin\theta/2$, where n and λ are the refractive index of the medium and wavelength of the incident light, respectively.

The spectrum obtained at $\theta = 10°$, however, is patently not related to the large-angle spectrum according to eq 1 and must arise from a different relaxation mode. This component may not arise from coupling of the translational diffusion process with the internal relaxation modes of rotational diffusion[8] or skeletal flexing[9] since these become important only at large scattering angles when $\kappa \cdot l > 1$.[8,9] In addition the spectrum recorded at $\theta = 30°$ cannot be fitted by a single Lorentzian but can be approximated by a two-Lorentzian fit such that the broad Lorentzian with halfwidth 350 Hz bears, within the relatively large experimental error, a quadratic dependence on scattering vector to the small-angle spectrum (hypothetical halfwidth at $\theta = 30°$ of 550 Hz) (Figure 2). We believe this clearly demonstrates that the relaxation mode giving rise to small-angle spectrum is a diffusion mode. We can, however, discount scattering from modes involving coupling of external diffusion to internal diffusive modes of the type involved in conformational transitions since these latter processes are much faster[4] than observed here. We have found in addition[10] that the wide-angle diffusion coefficient $\langle D_{\perp}\rangle_{\phi}$ varies with concentration in a nonlinear fashion from a value of 1.1×10^{-8} cm²/sec at a concentration of 0.1% to a value of 3.63×10^{-8} cm²/sec at a concentration of 0.01%. These results corroborate earlier measurements of the concentration dependence of the sedimentation velocity in these systems.[11]

On the basis of these observations, we have interpreted the results as indicating two external diffusion modes. Because of frequent intermolecular encounters and strong intermolecular interactions, unhindered rotational diffusion cannot occur. We propose that in close trajectories, the interacting polyacrylamide molecules tend to orient in a preferred parallel direction without however, forming an integrated complexed species. The macromolecules therefore behave as torsional oscillators or librators during these collisions. These dynamics we believe arise as a direct consequence of the two facts: firstly, the polyacrylamide chains are highly extended due to the intramolecular electrostatic repulsions of the carboxylate groups most of which are ionized at the pH of the solution; secondly, the possibility of extensive intermolecular interactions involving the hydrogen bonded networks between polymer and solvent which causes relative orientation of the molecules during collisions. The physical model of macromolecular motion which we envisage therefore corresponds to the macromolecular analog of the small molecule situation treated by Brot.[12] The macromolecular dynamics in such a system can be described by two partially averaged translational diffusion coefficients.

$$\begin{aligned}\langle D_{\parallel}\rangle_{\phi} &= 4.40 \pm 0.25 \times 10^{-7}\ \text{cm}^2/\text{sec}\\ \langle D_{\perp}\rangle_{\phi} &= 1.86 \pm 0.05 \times 10^{-8}\ \text{cm}^2/\text{sec}\end{aligned} \qquad (2)$$

The latter corresponds to the slow motion perpendicular to the molecular axis of the highly extended macromolecule and it is scattering from this mode that we have observed at large angles; the former characterizes motion parallel to the chain and corresponds to the small-angle spectrum. The polyacrylamide, note is highly polydisperse and the spectra can never be accurately approximated by a single Lorentzian. Thus the diffusion values[7] should be interpreted as molecular weight average values describing the mean dynamics of the two modes.

If we compute the equivalent hydrodynamic radii for the two diffusion modes, that is, the radii of spheres which would produce the same diffusion coefficients according to Stokes law, we obtain

$$\begin{aligned} r_{\text{equiv}}^{\text{paral}} &= 50\ \text{Å}\\ r_{\text{equiv}}^{\text{perp}} &= 1200\ \text{Å}\end{aligned} \qquad (3)$$

Now, a number of formulas exist[13] relating these equivalent radii to, for example, the values a, b, c, of an aniso-

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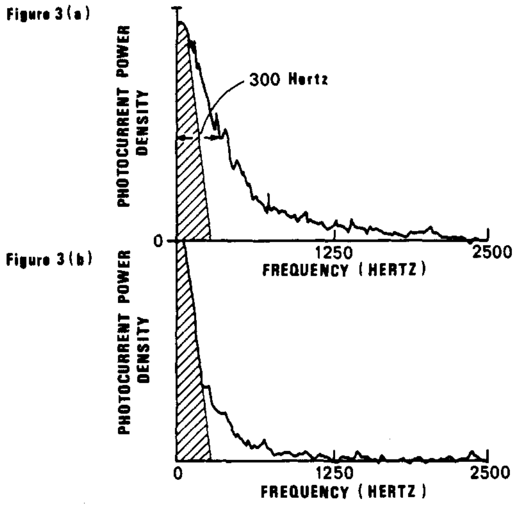

Figure 3. Square-root spectrum of 0.019% solution of Pusher-700*. (a) In deionized water at 26° and $\theta = 10°$. The shaded area indicates where scattering from the "transverse" diffusion mode will arise. Most of it is obscured by the zero-frequency spike of the spectrum analyzer. (b) In 0.5 *M* NaCl at 26° and $\theta = 10°$. The broad spectrum evident in part a has essentially disappeared.

metric molecule approximated as an ellipsoid with minor axes $a = b$ and major axis c, or to parameters describing a number of other geometries. Unfortunately, these formulas apply only to situations where intermolecular collisions are negligible and so we cannot at present obtain an idea of the gross macromolecular geometry of the polymer. Brenner,[14] has given a general formalism for the frictional coefficients of a system consisting of any number of interacting particles of arbitrary geometry moving through a fluid medium and we hope to use this analysis in later work to establish the exact molecular basis of the effect.

Finally as a critical test of our hypothesis that the low-angle spectrum arises from a diffusion mode parallel to the chain axis, and the wide-angle spectra from a diffusion mode perpendicular to the chain, we have examined the effect of ionic strength on the spectra. Increase in ionic strength results in a collapse of the highly extended conformation of the polymer[6] and consequently reduces the extent of intermolecular interactions. Figure 3 displays the square-root photocurrent spectra at $\theta = 10°$ and room temperature 26° of a 0.019% solution of the Pusher-700 (a) at low ionic strength as before and (b) in 0.5 *M* NaCl. The spectrum in Figure 3a has a halfwidth of 600 Hz and corresponds to a value of $\langle D_\parallel \rangle_\phi = 1.32 \pm 0.05 \times 10^{-7}$ cm²/sec. The shaded area in the spectrum represents where scattering from the "transverse" diffusional mode would occur.

When the ionic strength is raised, and the extended chain structure breaks down, the small-angle spectrum almost completely disappears as shown in Figure 3b. Also we have found that concentrations of NaCl and $CaCl_2$ equivalent to an ionic strength of 0.1 have an equally striking effect on the wide-angle spectrum which becomes much broader.[10] Thus, in the presence of 0.1 *M* NaCl the diffusion coefficient is 4.2×10^{-8} cm²/sec and, in the presence of 0.03 *M* $CaCl_2$, it is 5.7×10^{-8} cm²/sec. The larger diffusion coefficient in the Ca^{2+} solutions, incidentally, indicates that the effect is not simply an ionic strength effect in this system and in fact is excellent evidence for the conformation-directing properties of the bivalent Ca^{2+} ions which produce a much more compact molecular species. We regard this evidence as dramatic verification that the different spectra observed at small and large angles are indeed the result of scattering from two distinct diffusion modes which arise from highly hindered rotational diffusion due to frequent intermolecular encounters of the highly extended molecules and which merge on contraction of the polymer with increase in ionic strength.

A detailed study of the effect of molecular weight, concentration, temperature, and shear degradation of the polymer on these diffusive modes as well as large angle measurements designed to discover the rates of librational motion of the macromolecules is currently underway.

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