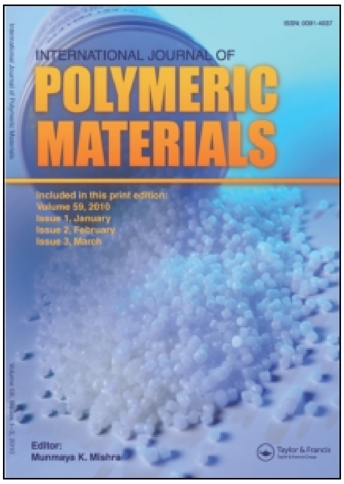

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# Studies of Conformational Changes and Intermolecular Interactions in Dilute Solutions of Partially Hydrolyzed Polyacrylamide by Optical Mixing Spectroscopy

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# Studies of Conformational Changes and Intermolecular Interactions in Dilute Solutions of Partially Hydrolyzed Polyacrylamide by Optical Mixing Spectroscopy†

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Moderately concentrated aqueous solutions of certain high molecular weight polyelectrolytes exhibit complex molecular relaxation modes in the range of 1 to $10^5$ $\sec^{-1}$ which confer useful commercial or biological properties. Although many different kinds of molecular relaxation phenomena have been proposed as causing the various unique properties of such solutions, the relative importance of the various modes remains unanswered mainly because of the lack of any accurate experimental means of studying these events. We describe a new laser light scattering technique which provides such a probe. We have used this method to study molecular dynamics, especially molecular transport processes, in dilute aqueous solutions of a partially ionized high molecular weight polyacrylamide. Two kinds of diffusion mode of the polymer are observed. This paper reports studies of the effect of ionic strength, polymer concentration and temperature on the slow diffusion mode.

## 1 INTRODUCTION

Dilute solutions of certain high molecular weight polymers exhibit complex viscoelastic properties in the frequency range 1 to $10^5$ $\sec^{-1}$. This behavior

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†Presented at the Midland Macromolecular Meeting on "Order in Polymer Solutions", August 20–24, 1973.

is characterized by a shear rate-dependent viscosity function which may exhibit a monotonic decrease (shear thinning) or increase (shear thickening) over some finite, though limited range of shear rate. Many of these systems have important commercial applications or play an important role in biological systems. Examples are dilute aqueous solutions of high polymers (such as partially-ionized polyacrylamides) whose properties of non-Newtonian flow through porous media are used to improve oil recovery efficiency in waterflood processes, and moderately concentrated aqueous solutions of proteins and polysaccharides (*e.g.* protoplasm) whose molecular dynamics determines the kinetics of important diffusion-controlled biological reactions. In general, the molecular relaxation modes which are the source of the non-Newtonian behaviour of these fluids, are poorly understood. There is agreement on the various kinds of molecular events which can contribute to these phenomena but not as to their relative importance.[1] In summary, the molecular dynamics of moderately concentrated polymer solutions can be regarded as dictated by a balance between intramolecular and intermolecular forces. The latter can be attractive, giving rise to microstructure formation (*e.g.* localized hydrogen-bonded networks), or repulsive (electrostatic). Strong intramolecular forces, whether attractive or repulsive, will usually cause conformational ordering of the polymer chains. According to the ideas of Eliassaf *et al.*,[2] a field of flow may shift this equilibrium towards more intermolecular interaction, depending on the relative strengths of the interactions, causing a "thinning" or "thickening" response respectively. Peterlin[3] has shown theoretically, however, that even in the absence of intermolecular forces, a shear thickening behaviour can be expected in dilute solutions of extended high molecular weight linear polymers due to the differential separation of polymer chain segments in a field of flow. Obviously, additional molecular factors such as the stiffness of the polymer chain or the strength of polymer-solvent interactions also play an important role.

One of the main reasons for the poor understanding of molecular dynamics in these systems of interacting macromolecules has been the lack of an accurate and direct means of investigating the various modes of molecular dynamic in the 1 to $10^5$ sec$^{-1}$ frequency range. A recently developed laser light scattering technique[4,5] which measures the frequency broadening of the scattered light due to the molecular motions of the scatterers offers the opportunity of unravelling at least the basic features of these relaxation modes. In what follows, we will first describe the technique and its application to these solutions of interacting macromolecules. We will then describe the results of some investigations of diffusion in dilute aqueous solutions of a 19.5% ionized polyacrylamide. In our initial studies of this system we have observed two quite distinct translational diffusion modes of the polymer.[6] We proposed a model to explain these unusual results which reflects the fact that the highly extended, charged molecules can only diffuse a small distance before encountering a near neighbor. For this reason, we believe the rotational diffusion of the molecules must be highly hindered and so they only have a liberational degree of freedom. Thus, because of frequent intermolecular encounters, and a balance of attractive (H-bonding) and repulsive (electro-static) intermolecular forces, the macromolecules oscillate in a cylindrical intermolecular field while diffusing, and so they exhibit two partially rotation-averaged diffusion modes.

These observations are discussed further in the light of more recent, additional evidence of the effect of concentration, temperature and addition of salts on the light scattering spectra related to the slower diffusion mode which we have labelled "transverse" diffusion.

## 2 QUASIELASTIC LASER LIGHT SCATTERING

Light scattered by a solution of macromolecules experiences small Doppler frequency shifts as a result of the relatively slow Brownian motions of the polymer chain segments which scatter the light. Pecora, in a series of papers,[7–10] has derived analytical expressions for the shape of the Rayleigh spectrum due to the various dynamic modes of the macromolecules. Briefly, these modes are: rotational and translational diffusion of the polymer, intramolecular flexing modes of the chains, and conformational transformations of the secondary structure of the macromolecules.

The Rayleigh spectrum $S(\boldsymbol{\kappa},\omega)$ from translational diffusion is a Lorentzian frequency distribution with halfwidth at half height $D_t\kappa^2$ where $D_t$ is the rotation-averaged translational diffusion coefficient and $\boldsymbol{\kappa}$ is the scattering vector:

$$S(\boldsymbol{\kappa},\omega) = \frac{\text{const.}}{\omega^2 + D_t\kappa^2} \tag{1}$$

As the scattering angle $\theta$ is varied, the linewidth of the spectrum therefore varies as the square of

$$|\boldsymbol{\kappa}| = 2nk_0 \sin(\theta/2) \tag{2}$$

where $n$ is the refractive index, $k_0 = 2\pi/\lambda_0$, and $\lambda_0$ is the wavelength of the incident light. Equation (1) is strictly true only for a monodisperse polymer sample; for a polydisperse sample, the spectrum will be more or less non-Lorentzian, depending on the width of the molecular weight distribution. To a good approximation, however, the linewidth will still vary quadratically with $|\boldsymbol{\kappa}|$ and be proportional to a statistical average diffusion coefficient.[11]

If the macromolecules are anisometric (*e.g.* an $\alpha$-helical polymer) with length $l$, then an additional Lorentzian component due to rotational diffusion appears with a halfwidth of the form $T_{\text{rot}} = D_t\kappa^2 + 6D_r$ where $D_r$ is the rotational diffusion coefficient.[7] For molecules which only scatter isotropically (which is true of the polyacrylamide sample we discuss later) this component only becomes important at large scattering angles when $\kappa \cdot l \geq 1$. Once again, if the polymer is polydisperse, the rotational component may be non-Lorentzian, but for moderate distribution widths, it should be possible to deduce an average value of $D_r$ by studying the angular dependence of the Rayleigh spectrum at large angles.

Semi-flexible polymers have a series of low-frequency skeletal vibration modes each characterized by a relaxation time $\tau_{vib}$ (*e.g.* the Rouse–Zimm model[12]). A Lorentzian spectral component with halfwidth proportional to $\tau_{vib}^{-1}$ will then appear at large scattering angles[10] (see also the work of Fujime *et al.*[13]). If the macromolecules are fluctuating between two conformational forms, a further component can arise due to relaxation through this equilibrium with halfwidth proportional to inverse relaxation time $\tau_c^{-1}$.[14–16] This relaxation time may be regarded as derived from an intramolecular diffusion term $D_{intra}$ and a nucleation term $\tau_n$.[15,16]

So far we have described the light scattering spectra to be expected for solutions of macromolecules in the limit of infinite dilution where intermolecular interactions are unimportant. At higher concentrations, in systems where strong intermolecular forces can occur, more complex relaxation modes of the polymer can occur involving the interaction of molecules during collisions or in close trajectories.

As we discussed before, in a system of the kind we are studying, where there is a balance of attractive and repulsive intermolecular forces between highly elongated macromolecules, the rotational degree of freedom of the polymer chains may be highly hindered due to frequent molecular encounters. The macromolecules may therefore exhibit two distinct partially rotation-averaged diffusion modes, one perpendicular to the molecular axis described by the diffusion coefficient $D_t^{\perp}$ and one parallel to the axis, described by diffusion coefficient $D_t^{\parallel}$. The presence of attractive forces also means that microstructural arrangements of molecules can spontaneously form in solution. The formation and disintegration of these structures will be described by a structural relaxation time $\tau_s$. Once again, this relaxation time may be composed of two terms, a nucleation term $\tau_n$ and a diffusion term describing growth and collapse of structured regions. Litowitz and co-workers[17] have studied the fast structural relaxation dynamics of associated liquids using interferometry to analyze the Rayleigh–Brillouin spectrum of scattered laser light. No studies of structural relaxation modes of polymers in moderately concentrated solutions have been attempted to our knowledge.

We have summarized the basic features of the molecular dynamics of interacting solutions of macromolecules. Since all of these modes contribute to the scattered light spectrum, how does one distinguish different processes from each other? This can only be done by studying the spectrum over the complete range of scattering angles and by varying the experimental conditions appropriately. Diffusion modes which involve spatial chain segment density gradients, whether internal (as in a conformational change) or external (as in normal translational diffusion or growth and decay of structured assemblies of chains), can be distinguished *a priori* from modes which do not involve spatial gradients. The former give rise to a spectral component whose linewidth varies linearly with the square of the scattering vector $\boldsymbol{\kappa}$ as shown in equation (1), while the latter cause angle-independent scattering. In addition, modes such as conformational transitions, skeletal flexing or structural relaxation will usually be much faster than translational or rotational diffusion modes. Also, by changing either polymer composition, or charge, or by varying solvent conditions, temperature, etc., it may be possible to choose between different modes to explain the spectral changes. By a judicious study, then, of the scattered light spectrum over a complete range of scattering angles and frequency shifts, and by studying the effect of changes in polymer and solvent environment, it is possible in principle to obtain a comprehensive description of the basic features of the molecular dynamics in these systems.

## 3 EXPERIMENTAL

### 3.1 Optical mixing spectroscopy

Because of the very small frequency shifts observed in Rayleigh spectra of polymer solutions, an indirect electronic scheme is used to detect the spectrum which utilizes the phenomenon of optical mixing in a phototube. Details of the method are well expounded in the literature,[4,5] and the optical mixing spectrometer used in these studies has also been well-described.[4b] In the experiments described below, the spectrometer was operated in the heterodyne mode.[4b]

### 3.2 Sample preparation

The polymer used in our experiments was a commercially available, high molecular weight, partially hydrolyzed polyacrylamide, marketed by the Dow Chemical Company as Pusher 700 polymer. Pusher 700 has a viscosity molecular weight of the order $10^6$ and is hydrolyzed to the extent of 19.5%. Aqueous solutions of the polymer were prepared by dilution with distilled, deionized water (equivalent to less than 0.02 ppm of NaCl) which had been filtered through 0.45μ Millipore to remove macroscopic debris. At the pH of solutions used, the polymer was essentially 100% ionized. Temperature of the solution in the scattering cell is controlled to better than 0.01°C.

# 4 RESULTS

In our initial studies of the angular dependence of the Rayleigh spectrum of 0.19 % aqueous solutions of Pusher 700, we found that the spectrum had two distinct components whose linewidths varied as the square of the scattering vector.[6] On the basis of the reasoning summarized above, we ascribed the component observed at large angles to partially rotation-averaged translational diffusion perpendicular to the molecular axis and the component observed more easily at small angles to diffusion parallel to the axis. Our model was supported by the disappearance of the small angle spectrum on raising the ionic strength. We have recent additional data on the effect of polymer concentration, temperature, and $Na^+$ and $Ca^{++}$ concentrations of equivalent ionic strength on the wide-angle spectrum.

## 4.1 Effect of polymer concentration

We measured the halfwidth of the 90° spectrum of Pusher 700 over the concentration range 0.1 % to 0.01 % at a temperature of 26°C. The variation of the computed diffusion coefficient over this concentration range is shown in Figure 1. It is evident that the diffusion coefficient varies in a non-linear fashion and cannot be assumed independent of concentration at the highest dilutions we could study. The large increase in diffusion coefficient with dilution reflects the strong influence of intermolecular forces on the friction coefficient of the polymer.

## 4.2 Effect of temperature

We studied the changes in spectral linewidth at a scattering angle of 60° over the temperature range 14°C to 40°C of a 0.025 % solution of Pusher 700. The results are summarized in Table I. Within experimental error, there is a decrease of the diffusion coefficient as the temperature increases which is, of course, exactly opposite to the result one might expect from a Stokes–Einstein kind of model.[4a] This perplexing result makes some sense if one uses the arguments of Kanevskaya *et al.*[18] who ascribed the positive temperature coefficient of viscosity in concentrated polymethacrylic acid solutions to an increase in the number of intermolecular hydrogen bonds with temperature. Thus the negative temperature dependence of our wide angle diffusion mode, can be explained on the basis that the increased frequency of intermolecular collisions with temperature results in an increase in the number of intermolecular hydrogen bonds formed during close trajectories and a corresponding increase in the friction coefficient.

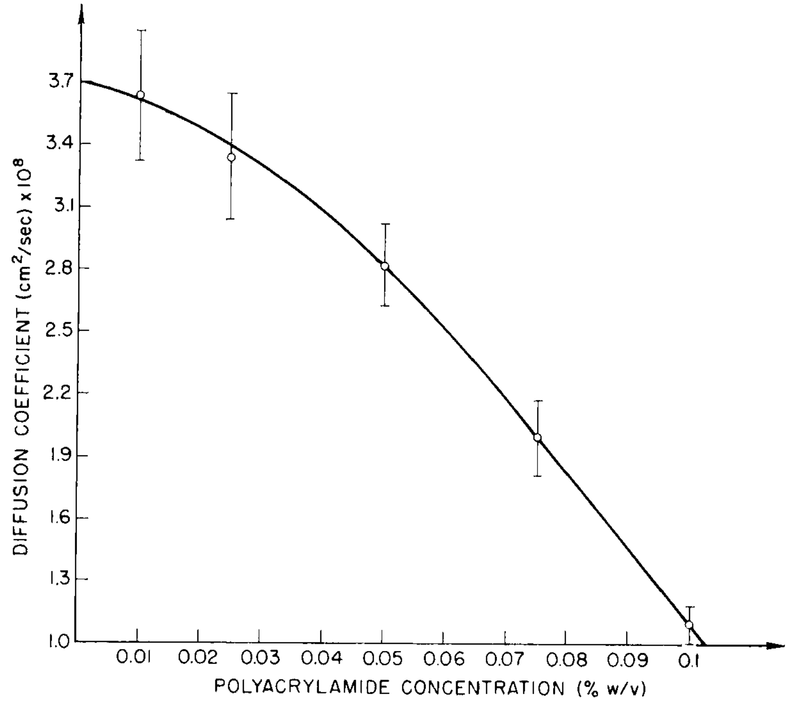

FIGURE 1 Concentration dependence of the "transverse" diffusion coefficient of Pusher 700 over the concentration range 0.1 % to 0.01 % at 26°C.

TABLE I

Temperature dependence of the Rayleigh linewidth of 0.025 % Pusher 700 at $\theta = 60°$

| $T^a$ (°C) | $\Delta\nu_{1/2}{}^{sqrt\ b}$ (Hz) |
|---|---|
| 14.0 | 650 |
| 19.5 | 604 |
| 26.0 | 620 |
| 40.0 | 508 |

[a] ±0.5°C.
[b] ±15 Hz.

### 4.3 Effect of salt concentration

In earlier work we showed that when a 0.025 % solution of Pusher 700 was made 0.1 *M* in NaCl, the small angle mode disappeared. We have also studied the effect of $Na^+$ and $Ca^{++}$ concentrations of ionic strengths equivalent to 0.1, 0.01 and 0.001 on the 90° scattering spectrum of 0.05 and 0.25 % solutions of Pusher 700. Figure 2 shows the effect of $Ca^{++}$ and $Na^{+}$ concentrations of ionic strength 0.1 on the 90° square root Rayleigh spectrum of 0.05 % Pusher 700. It is obvious that the presence of salt has drastically broadened the spectrum. It is equally apparent that the spectrum in the presence of $Ca^{++}$ is substantially broader than the $Na^{+}$ spectrum, indicating a larger diffusion coefficient and hence a smaller hydrodynamic radius. Since the ionic strengths are equal, this result demonstrates that the $Ca^{++}$ ions have a specific conformation directing effect on the polyacrylamide, not merely the dielectric effect of collapsing the structure because of a reduction in electrostatic repulsions along the chains. Table II summarizes all the data on salt effects. The results for the 0.025 % solution are nearly the same as those for the 0.05 % solution indicating that intermolecular effects are essentially absent in the presence of salt. Also, the salt effect has largely disappeared at ionic strength 0.01 and completely absent at 0.001 ionic strength. Figures 3, 4 and 5 show single Lorentzian curve fits to the squared spectra of Figure 2. An excellent fit over the whole spectrum was obtained for the $Ca^{++}$ spectrum of Figure 4 but not quite so good for the other two. This reflects the fact that

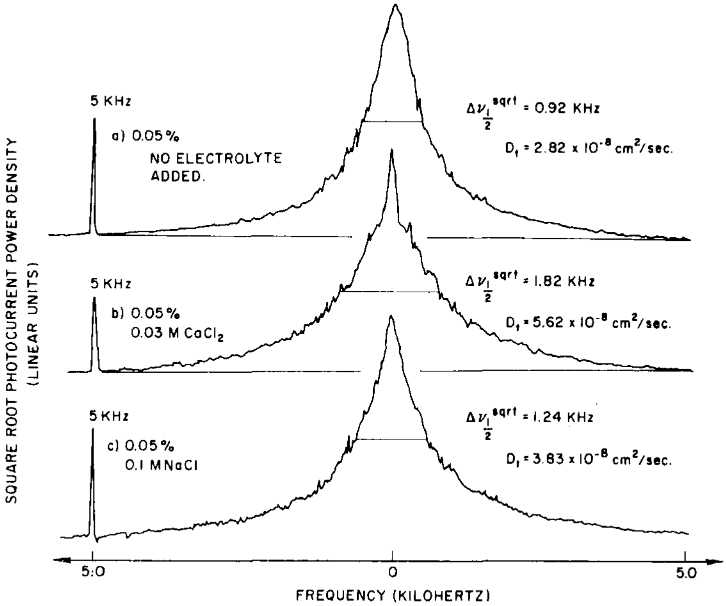

FIGURE 2 Effect of ionic strength on the 90° scattering spectrum of a 0.05 % solution of Pusher 700. Broadening of the spectrum indicates an increase in diffusion coefficient and therefore a decrease in effective hydrodynamic diameter of the macromolecules.

TABLE II

Effect of ionic strength on the "transverse" or slow diffusion mode of Pusher 700 at 26°C.

| System | $\Delta\nu_{1/2}^{sqrt}$ (KHz) | $D_t \times 10^8$ (cm$^2$/sec) |
|---|---|---|
| P-700: 0.025% + 0.1*M* NaCl | 1.37 | 4.23 |
| 0.025% + 0.01*M* NaCl | 1.11 | 3.43 |
| 0.025% +0.001*M* NaCl | 0.93 | 2.87 |
| 0.025% + 0.03*M* $CaCl_2$ | 1.86 | 5.74 |
| 0.025% + 0.003*M* $CaCl_2$ | 1.16 | 3.59 |
| 0.025% + 0.0003*M* CaCl | 0.98 | 3.03 |
| 0.05% + 0.1*M* NaCl | 1.24 | 3.83 |
| 0.05% + 0.03*M* $CaCl_2$ | 1.82 | 5.62 |
| 0.05% neutral solution | 0.92 | 2.80 |

Note: Ionic strength of 0.1 *M* NaCl and 0.03 *M* $CaCl_2$ is 0.1. Dilution by a factor of 10 decreases ionic strength by a factor of 10.

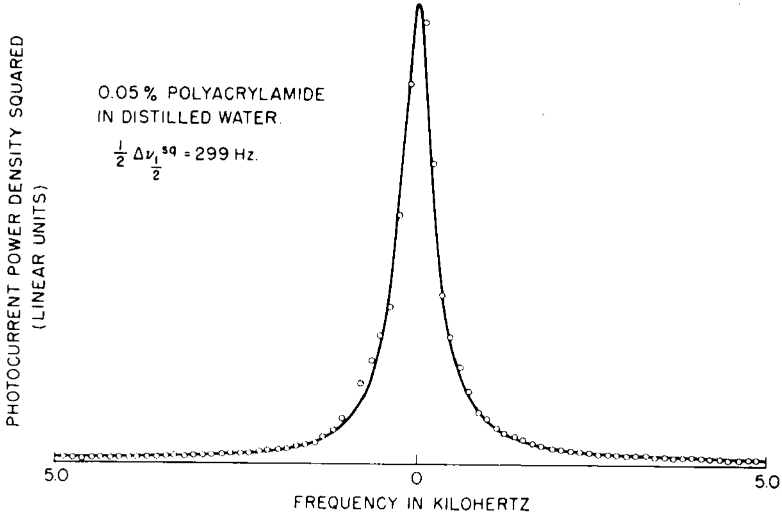

FIGURE 3 Single Lorentzian fit to squared points on the spectrum shown in Figure 2(a): 0.05% Pusher 700 in solution at low ionic strength.

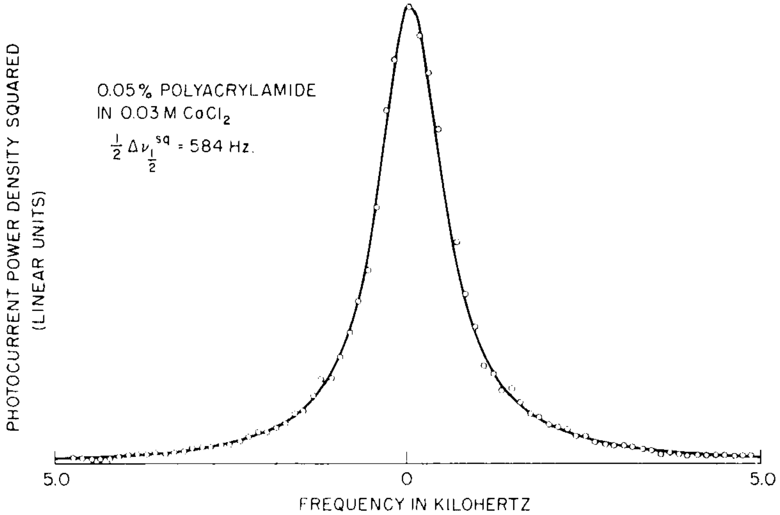

FIGURE 4 Single Lorentzian fit to squared points on the spectrum of Figure 2(b): 0.05% Pusher 700 in 0.03 *M* $CaCl_2$. We have omitted points on the local oscillator spike of the spectrum analyser clearly visible in Figure 2(b).

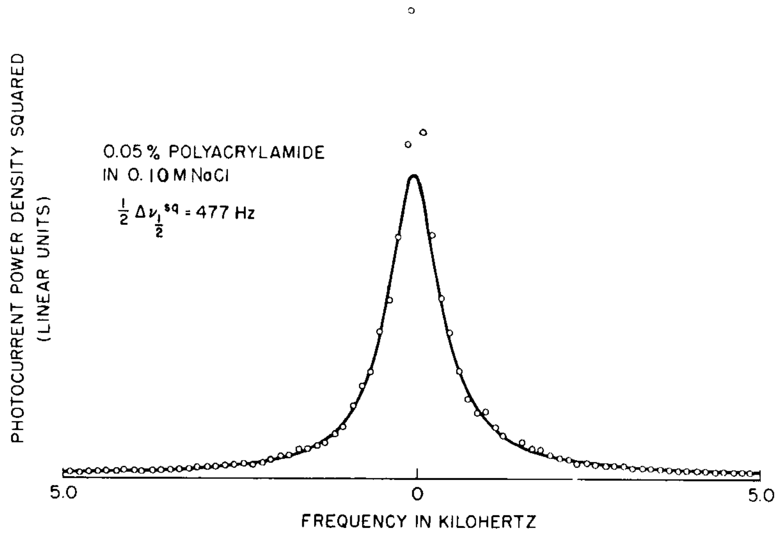

FIGURE 5 Single Lorentzian fit to squared points on the spectrum of Figure 2(c): 0.05% Pusher 700 in 0.1 *M* NaCl.

the $Ca^{++}$ ions have produced a much more homogeneous distribution of macromolecular sizes than is found in the neutral solution or in the presence of $Na^{+}$, reinforcing the observation of the strong conformation directing effect of $Ca^{++}$.

## 5 DISCUSSION AND CONCLUSIONS

The results summarized in the previous section leave no doubt that the process of molecular transport in dilute, aqueous solutions of partially-ionized polyacrylamide is highly perturbed by the presence of strong intermolecular forces, even in the most dilute solutions amenable to study (0.001 % w/v). Thus, our observations of the increase in diffusion coefficient with dilution, and the negative temperature coefficient of diffusion, indicate that attractive forces (hydrogen bonding) brought into play during intermolecular encounters increase the frictional coefficient of the molecules. Increasing the ionic strength of the solution has two effects: first of all, the electrostatic repulsions of the ionized groups along the polymer chains are drastically reduced causing a collapse of the extended conformation of the molecules; second, the ions disrupt the hydrogen-bonded network which tends to form during molecular encounters and thus banish the effect of hydrogen-bonding on the viscous drag of the molecules. Both of these effects result in a large increase in the diffusion coefficient of the macromolecules with ionic strength. In addition, we have clear evidence that the presence of $Ca^{++}$ ions has a specific conformation-directing effect on the polyacrylamide since they produce a much larger collapse of the polymer (large increase in diffusion coefficient) than corresponding ionic strengths of $Na^{+}$ ions. These conclusions are reinforced by our curve fitting results of Figures 3 to 5.

The data reported here further support our anisotropic model for diffusion in the partially-ionized polyacrylamide system. The disappearance or at least the substantial narrowing of the small angle spectrum and the dramatic broadening of the wide angle spectrum with increase in ionic strength of the solvent indicate that our two observed partially rotation-averaged diffusion modes merge into a single completely averaged mode because of the reduction in intermolecular encounters and decrease in hydrogen-bonded interactions between molecules.

It must be emphasized, however, that while we have ample support for our anisotropic diffusion model, it cannot be regarded as definitively established, since other explanations are feasible. For example, we cannot be certain that the fast diffusion component seen at small angles is not related to the dynamic growth and decay of transient hydrogen-bonded polymer networks in the solution. We have rejected this conclusion largely on the basis that polymer chains with a high charge density are not likely to form structured assemblies in solution. In order, however, to definitely exclude this possibility, further work must be done to study the effect of polymer structure, degree of ionization, solvent, and a more detailed investigation of the angular dependence of the Rayleigh spectrum.

In summary, we have described a novel laser light scattering approach to the problem of experimentally observing macromolecular dynamics in non-dilute solutions where intermolecular forces modify the relaxation spectrum. We note that many commercially important polymer solutions as well as biological fluids derive their viscoelastic properties from the interaction of the dissolved macromolecules. Light scattering data has been presented which leads to the conclusion that the effect of a balance of attractive and repulsive intermolecular forces in dilute solutions of a partially-hydrolyzed polyacrylamide is to produce two partially rotation-averaged diffusion modes. An important consequence of this initial series of measurements is that they cast some doubts on purely unimolecular models, such as that proposed by Jones and Davies[19], of the mechanism of action of these polymers in increasing the efficiency of waterflood oil recovery, since even at highest dilutions we have found evidence of close intermolecular hydrodynamic coupling.

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## DISCUSSION

**Prof. L. Tiffany** (*University of Michigan, Ann Arbor, Michigan*): Have you applied this optical mixing spectroscopy to polypeptides?

**Prof. A. M. Jamieson:** Yes, we have done studies of conformational (size) changes in polypeptide systems [*e.g., Biopolymers* **11,** 2267 (1973)] but not at the very high molecular weights of the polyacrylamide system where intermolecular interactions become important.

**Dr. M. Shinohara** (*Dow Corning, Midland, Michigan*): The difference in the effect of $Na^+$ and $Ca^{++}$ ions on the diffusion constant of partially hydrolyzed polyacrylamide will be more readily understood if the effect of $Li^+$, $K^+$ or $Cs^+$, or $Mg^{++}$ or $Ba^{++}$ ions is known. Have you performed such studies in the presence of other salts than NaCl or $CaCl_2$? Don't you think electrolytic conductance gives you some insights in elucidating the effects of salts?

**Prof. A. M. Jamieson:** We have not yet studied the effects of salts other than NaCl or $CaCl_2$ on diffusion of partially hydrolyzed polyacrylamide. It is true that such studies will be necessary to elucidate the importance of such factors as cation size or degree of cation solvation on the conformational change of the polymer. It seems to me also that measurements of ionic conductance in these solutions should throw light on the strength of binding of the ions to the polymer, but we have not tried such experiments to date.

**Dr. F. B. Bruschtein** (*Dow Chemical Company, Midland, Michigan*): I have measured viscosities of these polymers in presence of monovalent and divalent counterions. The effect of divalent counterions was strikingly different: with increasing ion concentration, the viscosity first increased and then decreased. The most efficient was $Mg^{++}$, then $Ca^{++}$. The monovalent ions did not show such effect at the low salt concentrations studied. Did you observe any change in the temperature dependence of the diffusion coefficient when you did your work in presence of salts?

**Prof. A. M. Jamieson:** No work has been done.

**Dr. Bruschtein:** Do you expect an increase of the diffusion coefficient in presence of salt, especially $Ca^{++}$? Do you expect increase in the diffusion coefficient with temperature in the case of extremely diluted solutions?

**Prof. A. M. Jamieson:** In the presence of salts, I would indeed expect increase of the diffusion coefficient with temperature and at extremely high dilutions when intermolecular effects are no longer observed, I would also expect this behavior.