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Decay Time Distributions from Dynamic Light Scattering for Aqueous Poly(vinyl alcohol) Gels and Semidilute Solutions

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ABSTRACT: Dynamic light scattering has been used to obtain decay time distributions for permanent poly(vinyl alcohol) (PVA) gels and the corresponding semidilute solutions by Laplace inversion of the autocorrelation functions. The gels were prepared from aqueous solutions of the narrow distribution polymer by cross-linking using glutaraldehyde. The PVA concentration range extends up to 7% w/v; parallel measurements were made on the gel and corresponding solution as a function of temperature between 3 and 55 °C. Two main relaxational modes typified the PVA solutions, both relaxation rates being diffusive. The fast relaxation characterizes the diffusive motions in the transient gel formed by interpenetration of molecular domains. The slow mode is considered to derive from "clusters" or (groups of chains) having a size that depends on concentration and only slightly on temperature. Formation of the permanent gel resulted in disappearance of the slow mode, and the gels were characterized by single-exponential correlation functions. At a given concentration, the polymer–polymer correlation length of the gel was almost twice that characterizing the transient network in the solution in spite of a very low cross-linking level (≈1%). In both systems the diffusion coefficient is linearly dependent on concentration. At high cross-linking density the correlation length shows a marked decrease.

Introduction

Early work dealing with the dynamic light scattering of permanent networks showed that the hydrodynamic modes of the corresponding solution are inhibited by cross-linking and that the gel mode contributes the major part of the dynamic light scattering. In terms of network structure, the cooperative diffusion coefficient (D_c) is inversely proportional to the polymer–polymer correlation length (ξ), defining the average distance between cross-links according to

$$D_c = kT/6\pi\eta_0\xi \qquad (1)$$

The cooperative diffusion coefficient obeys a scaling law with concentration similar to that found for semidilute solutions[1,2] of the corresponding polymer. Nevertheless, apart from the scaling similarity, a closer comparison of the dynamic behavior of gels and solutions does not seem to have been made. The choice of gel is central to such a comparison. The early work on polystyrene gels was based on networks prepared by anionic block copolymerization of styrene with divinylbenzene (DVB), so that each portion of linear chain connects branch points made up of DVB nodules, each having appreciable dimensions.[1,2] The functionality of the cross-links is unknown. Because of the readiness with which they may be prepared, their high optical clarity, and their commercial importance, substantial work has been done on water-swollen polyacrylamide (PAA) gels.[4-18] However, it would appear that PAA gels may, depending on the preparation technique used, be structurally inhomogeneous and contain large interconnected spaces interspersed with regions with a fine gel mesh.[8,13,15] Our preliminary experiments support this, and DLS measurements furthermore substantiate a complex distribution of relaxation times in the corresponding PAA solutions (prepared in an identical manner to the gels but without bisacrylamide). For this reason a different route to gel preparation was chosen. In order to get around these structural deficiencies, which accompany gelation when starting from the monomer, we have examined poly(vinyl alcohol) (PVA) gels prepared by directly cross-linking the polymer in aqueous solution using glutaraldehyde at low pH according to the procedure of Horkay et al.[19,20] The density of cross-links is sparse. This system was deemed convenient for comparing the dynamic behavior of solutions and gels since the chains are well-defined. Also (in the presence of magnesium perchlorate) the gels are stable in dimensions, and when gelation is carried out on the ultrafiltered solutions, glass-clear gels exhibiting no significant angular dissymmetry of the scattered light are always obtained. This is important since a particular difficulty in working with gels has almost invariably been the ambiguity accompanying partial heterodyning deriving from suspended particles and/or air bubbles.

We have utilized a broad-band autocorrelator (23 simultaneous sampling times) and methods for performing Laplace inversion which yield the "complete" (from the point of view of the light-scattering experiment) distribution of decay times. This aspect differentiates the present study from earlier ones. The latter employed either a forced single-exponential fit or the method of cumulants, both of which are unsuitable for DLS data analysis in systems with a broad spectrum of decay times. The polymer concentration range was limited to the region corresponding to semidilute solutions; i.e., $C > C^*$ but not exceeding $C = 0.1$ g mL^{-1}. A parallel series of semidilute PVA solutions was prepared for comparison purposes.

A further attractive feature of these gels is that they may be fully acetylated and they then become susceptible to examination in nonaqueous media, for example, methanol (which is a Θ solvent for poly(vinyl acetate) at 6 °C) and acetone, which is a thermodynamically good solvent. It thus becomes possible to examine the role of solvent quality on the dynamic behavior of the same gel structure. It may also be noted that Horkay et al.[19-21] have made very comprehensive studies of the mechanical properties of both PVA and PVAc gels prepared in an identical manner.

Experimental Section

Poly(vinyl alcohol) was purchased from BDH Chemicals, Ltd., UK. A purification procedure was used. The polymer was dissolved at a concentration of 0.1% in distilled water and

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filtered through a G-3 glass filter, followed by centrifuging at 35 000 rpm in a Beckman preparative ultracentrifuge.

The polymer was precipitated by using acetone, redissolved in water, and reprecipitated with acetone. The PVA was finally obtained by freeze-drying a dilute aqueous solution. The molecular weight of this material was determined by intensity light scattering (using the technique and instrumentation described in ref 23). A value of M = 110 000 was found.

Preparation of PVA gels was carried out following essentially the procedure described by Horkay et al.[19] Solutions of the PVA were made up in 0.03 M HCl (pH 1.5) and filtered through 0.22-μm Millipore filters. The solutions were filtered directly into light-scattering ampules (cylindrical, 10-mL glass cuvettes of 15-mm o.d.) and sealed.

Cross-linking was accomplished by addition of aqueous glutaraldehyde solution (5% aqueous solution). The ratio of the number of moles of cross-linking agent to the monomer unit of the polymer was varied between 0.25% and 1.25%. Most measurements were made (except as otherwise stated) on gels with 1% monomer cross-linking agent. The temperature was held at 10 °C to slow down the reaction, yielding bubble-free solutions. However, it was found that the initially glass-clear gels slowly (over a period of days) clouded and contracted to produce a supernatant layer of solvent. It was found that this could be circumvented by the addition of 0.5 M magnesium perchlorate to the PVA solution prior to cross-linking.[22] The resulting gels maintain their physical dimensions and clarity. To check whether the presence of the salt influences the hydrodynamic properties of the polymer, viscosity measurements (below) were made on solutions of PVA in the absence and presence of magnesium perchlorate over the PVA concentration range up to 10% w/v. Identical viscosities were obtained. Thus all solutions (containing magnesium perchlorate) were divided into two portions, one of which was cross-linked and the other of which was retained for the comparison between gels and solutions.

Macroscopic shear viscosities were measured on the PVA solutions using a Bohlin VOR rheometer. The measurements were made over the concentration range up to 10% w/v as a function of shear rate at 25 °C. Viscosities of PVA were found to be shear rate independent.

Intrinsic viscosity measurements were made on dilute PVA solutions at 25 °C using an Ubbelohde capillary viscometer. A value of 0.95 dL g^{-1} was obtained.

Dynamic light-scattering measurements have been made by using the apparatus and techniques described in ref 23. All solutions were filtered through Millipore filters (0.22 μm) prior to sealing into light-scattering cuvettes.

Laplace inversion of the autocorrelation curves was performed by using a constrained regularization program REPES[24] to obtain the distribution of decay times over about 8 decades in delay time. The algorithm differs in a major respect from CONTIN[25] in that the program directly minimizes the sum of the squared differences between the experimental and calculated $g^2(t)$ functions by using nonlinear programming, and the a priori chosen parameter "probability to reject" was selected as P = 0.5. The decay time distributions were similar to those obtained using CONTIN with a similar degree of smoothing.

Results and Discussion

Semidilute solutions of PVA were prepared in the concentration range 1–7% (where the overlap concentration C^* = 1%, by using as the definition $C^* = 1/[\eta]$). The decay time distributions at different angles are shown in Figure 1 for some selected concentrations. With increasing concentration, the faster mode decreases in relative amplitude such that at the highest concentrations the intensity of the slower mode dominates the scattering almost completely (Figure 2) and moves to progressively longer relaxation times. The distributions at intermediate concentrations indicate that a bimodal model would be an oversimplification since there are small relative amplitudes of components with smaller size. A dominant slow mode has been shown to exist in semidilute solutions of poly(ethylene oxide) in water,[26,27] as well as in methanol[23] and other solvents. Burchard and Eisele[28] also reported a similar phenomenon for poly(vinylpyrrolidone) (PVP) in aqueous solution and ethanol solution, both of which are good solvents for PVP. Similar phenomena have been described for poly(methacrylic acid) in aqueous solution[30] but even for polystyrene in ethyl acetate.[39]

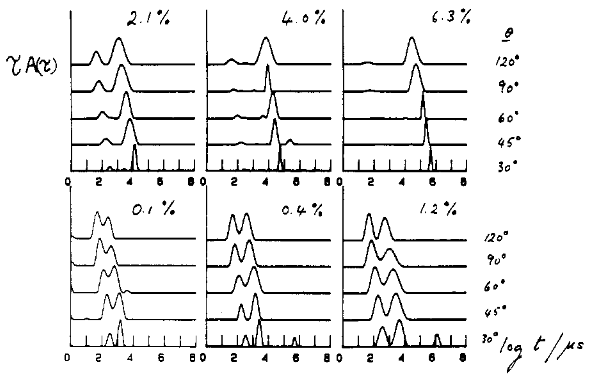

Figure 1. Decay time distributions for aqueous PVA solutions at the concentrations and angles shown (25 °C). The vertical axis is $\tau A(\tau)$ to give an equal-area representation. The fast mode corresponds to the "blob" diffusion and the slow to the translational mobility of clusters of chains.

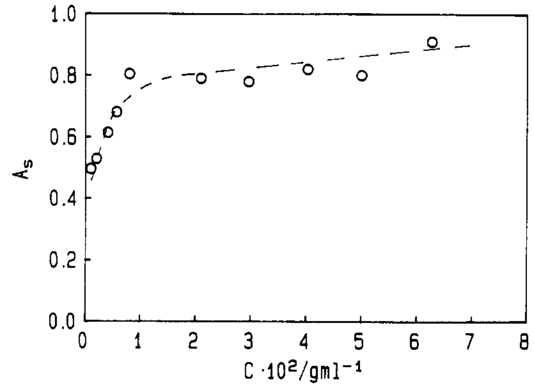

Figure 2. Relative amplitude of the slow-mode data in Figure 1 shown as a function of PVA concentration. Angle = 30°, and data are for 25 °C.

The two major modes observed, for example, at C = 1.2%, are both q^2-dependent as shown in parts a and b of Figure 3 in plots of the relaxation rate (Γ) versus $\sin^2(\theta/2)$ for the fast and slow modes at various concentrations.

Characteristics of the Slow Mode in PVA Solutions. The dominant slow peak is considered to describe the mobility of clusters of chains (or ordered domains interspersed with disordered regions), while the fast mode is considered to correspond to the collective motions of the transient network.

It should be emphasized that cluster formation appears to typify systems involving polar polymers which can associate or order through, for example, participation of hydrogen bonding. Clustering does not appear to be prevalent with polymers in thermodynamically good, nonaqueous solvents for which the cooperative mode is almost the sole dynamic component in the scattering from semidilute solutions.

As has been shown by Benmouna et al.,[29] two diffusive modes become observable in the light-scattering experiment when there is, for example, size polydispersity present such as in a polymer 1/polymer 2/solvent ternary mixture where polymers 1 and 2 are identical chemically and differ only in molecular size. The signal from one species is modulated by the second, leading to a bimo-

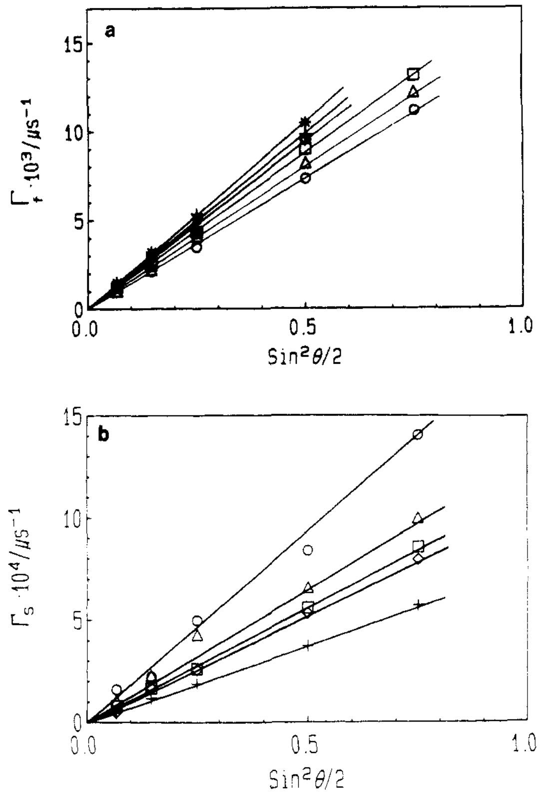

Figure 3. Relaxation rate, Γ, as a function of angle at 25 °C. (a) Fast mode: (○) 2.1%; (△) 3.0%; (□) 4.0%; (◇) 5.0%; (+) 6.3%; (*) 6.8%. (b) Slow mode: (○) 0.1%; (△) 0.21%; (□) 0.41%; (◇) 0.57%; (+) 0.81%. The data have been derived from the moments of the peaks corresponding to decay time distributions as shown in Figure 1.

dal autocorrelation function. The two relaxation rates observed correspond to the cooperative diffusion coefficient (D_c) on the one hand and the interdiffusion coefficient on the other. At sufficiently low concentration the interdiffusion coefficient will become equal to the self-diffusion coefficient.[43]

Figure 4a shows the slow-mode data at different temperatures, corrected by using the solvent viscosity and absolute temperature. These data lie on a common curve as is anticipated for translational diffusion if the particle size is unchanged with temperature. This is approximately the case as also shown in Figure 6b. The reduced diffusion coefficient decreases very strongly with increasing concentration. This decrease does not follow a simple power law.

Figure 4b represents the slow-mode diffusion coefficient corrected for the solution viscosity. The strong negative slope ($D_s\eta_s/T = -1.18C + 9.2$) shows qualitatively that the clusters grow in size with increasing concentration. Values of the hydrodynamic radius (R_h) of the slow component in the PVA semidilute solutions evaluated by using the Stokes–Einstein equation are shown in Figure 4c (although as shown by Phillies[30] in experiments on latex particles diffusing in polymer solutions this equation may not always be a reliable means of estimating particle dimensions at finite concentrations). An alternative is also possible. Sedlak et al.[31] have shown that from plots of the angular dependence of the relative intensities of the fast and slow modes in the DLS experiment in semidilute solutions one may estimate an apparent radius of gyration (R_g). This may be justified when the fast component corresponds to the network mode of the semidilute solution, and its amplitude should then be angle-independent. The angular variation of (A_f/A_s) should then be only related to the size of the slow diffusive component. This approach was used to examine clusters in poly(methacrylic acid) and has recently[23] been used to elucidate the characteristics of the clusters formed in PEO solutions in methanol. Examples of these plots are given in parts a and b of Figure 5, and the resulting apparent radii of gyration are shown as a function of concentration in Figure 6a and as a function of temperature in Figure 6b. R_g shows a modest increase from around 600 Å at $C = 1\%$ to about 1100 Å at 7%. This change is smaller than that indicated in Figure 4c. For comparison we note that an approximate estimate of R_g for the single PVA coil, obtained from the intrinsic viscosity by using the Flory–Fox equation, gives a value of 150 Å at infinite dilution. (This value corresponds to a persistence length of about 23 Å and an overlap concentration of $C^* \approx 1.3\%$, where $C^* = 3M/4\pi R_g{}^3N_A$.) From the dominant scattering of the slow mode at the higher concen-

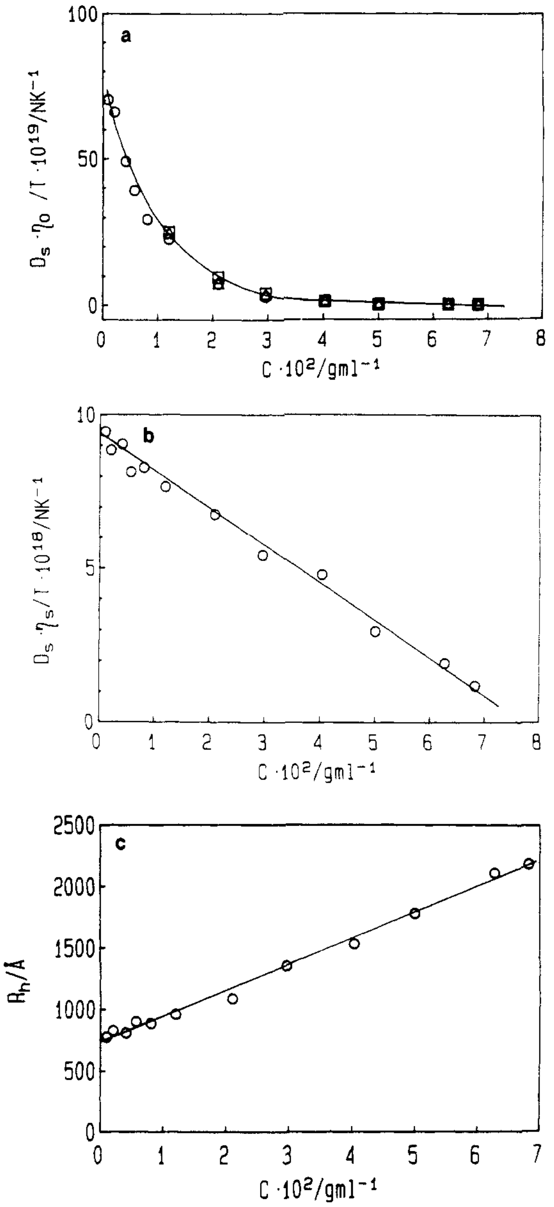

Figure 4. (a) Slow-mode diffusion coefficient at three temperatures (25 °C (○); 10 °C (□); 3 °C (△)), corrected for temperature and the corresponding solvent viscosity, as a function of PVA concentration. (b) Slow-mode diffusion data at 25 °C, corrected for the solution viscosity, plotted against PVA concentration. (c) Values of the hydrodynamic radius for the slow component in PVA semidilute solutions, estimated by using the Stokes–Einstein equation together with the solution viscosity, η_s. ($R_h = kT/6\pi\eta_s D_s$).

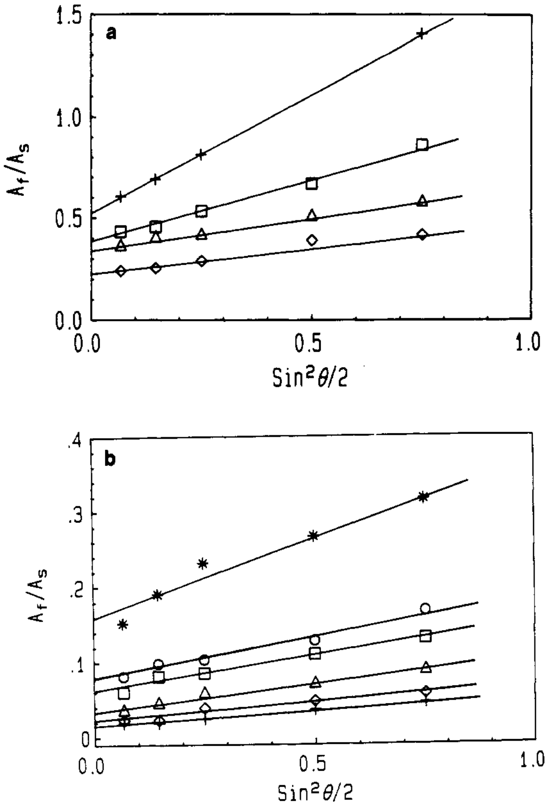

Figure 5. (a) Ratio of relative amplitudes (A_f/A_s) versus angle for dilute solutions at 25 °C: (+) 0.1%; (□) 0.41%; (△) 0.57%; (◇) 0.81%. (b) Corresponding plot at semidilute concentrations: (*) 2.1%; (○) 3.0%; (□) 4.0%; (△) 5.0%; (◇) 6.3%; (+) 6.8%.

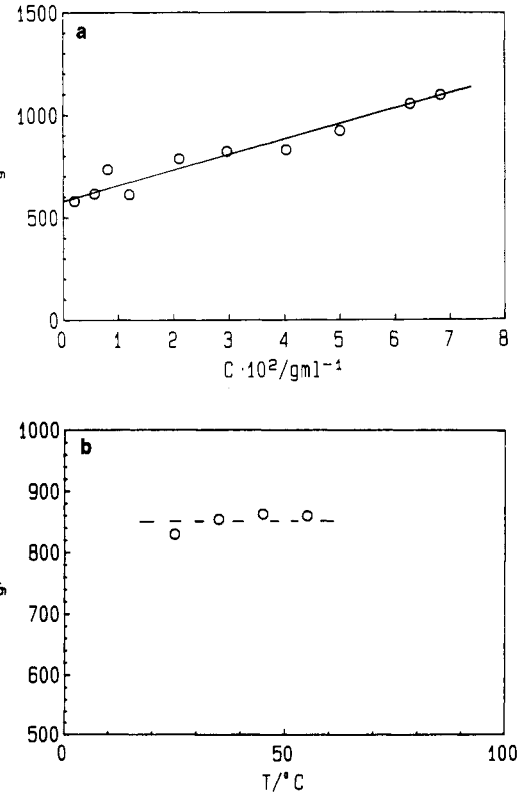

Figure 6. (a) Values of apparent radii of gyration (R_g) for the slow mode evaluated from plots a and b of Figure 5 as described in the text. (b) Apparent radii of gyration for the slow mode versus temperature for a PVA solution; concentration 4.0%.

trations, one may surmise that the number of such clusters also increases strongly with concentration.

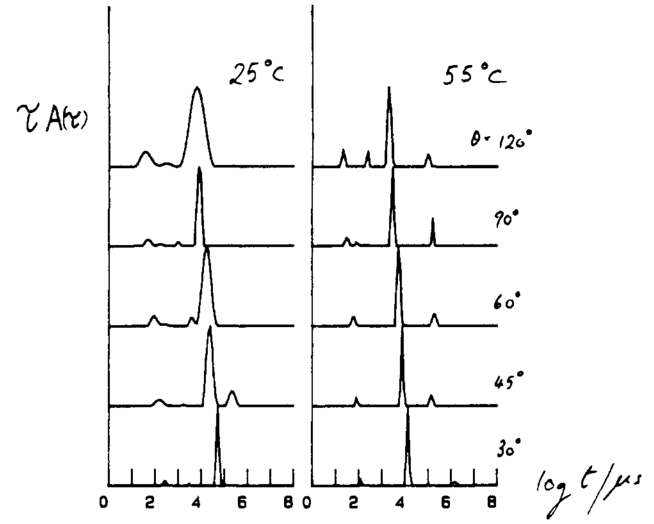

Figure 7. Comparison of decay time distributions as a function of measurement angle for a semidilute PVA solution (C = 4.03%) at (a) 25 °C and (b) 55 °C.

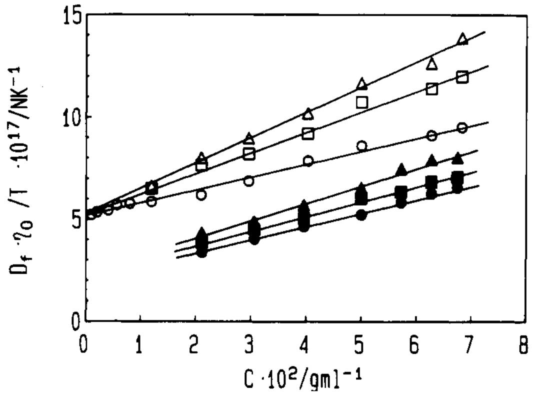

Figure 8. Diffusion coefficients for the fast mode, corrected for temperature by using the ratio η_0/T, as a function of PVA concentration in solutions (open points) and the permanent gels (filled points). η_0 is the solvent viscosity and T the absolute temperature (triangles, 25 °C; squares, 10 °C; circles, 3 °C).

Figure 7 compares distributions as a function of measurement angle for a sample with C_{PVA} = 4.03% at the temperatures 25 and 55 °C. With increasing wave vector the fast gel mode increases in relative amplitude and an intermediate component is apparent. At the higher temperature, a very slow mode of small amplitude is also present.

Network Mode in PVA Semidilute Solutions. The temperature-corrected diffusion coefficient for the fast mode, characterizing the network above C^*, shows, within experimental uncertainty, a linear increase with concentration (Figure 8). The hydrodynamic radius of the coil (R_h), calculated from the infinite dilution intercept in Figure 8 by using the Stokes–Einstein equation together with the solvent viscosity, has the value 140 Å. For both gels and solutions, the slope is greater at lower temperature, which is in agreement with expected trends in solvent quality. It is well-established that the heat of mixing of hydrogen-bonding solutes and water is typically exothermic (i.e., solubility decreases with increasing temperature as does the swelling of hydroxylic gels.[33,34] The differences in slope are less pronounced with the gels as would be anticipated since the cross-links restrict the volume available to the polymer chains.

It may be seen in Figure 9 that the dynamic correlation length decreases with decreasing temperature and the solvent quality improves. (It is typical, for example,

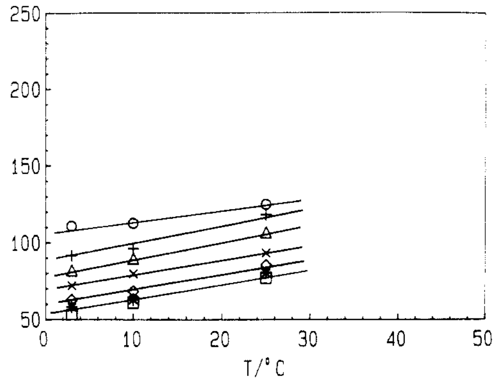

Figure 9. Correlation length evaluated by using eq 1 for the fast-mode data in PVA solutions: (○) 1.2%; (+) 2.1%; (△) 3.0%; (×) 4.0%; (◇) 5.0%; (*) 6.3%; (□) 6.8%.

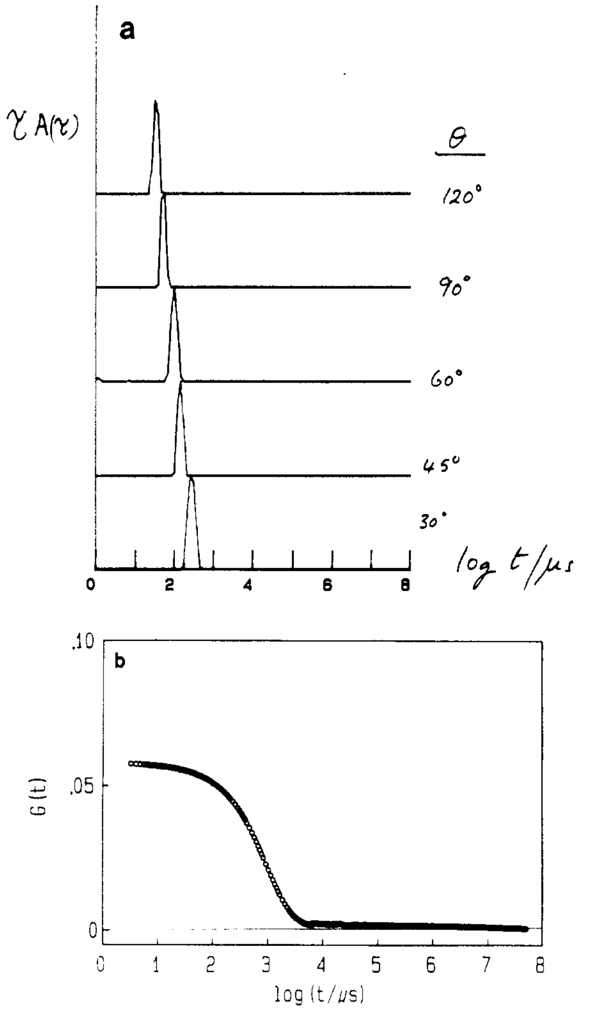

Figure 10. (a) Decay time distributions for the permanent gel (C = 5.0%) at various measurement angles and 25 °C. (b) Autocorrelation curve for a permanent gel (C = 3.06%) at 25 °C and measurement angle 30°.

of most polar, water-soluble polymers that the intrinsic viscosity has a strong negative dependence on temperature.[35]) This also provides a sensitive index of changes in solvent quality. For most flexible polymers in nonaqueous solvents the opposite behavior is found. The concentration exponent, obtained from the plots in Figure 11, has the surprisingly low value of −0.39, compared with the exponent for the permanent gel (−0.72).

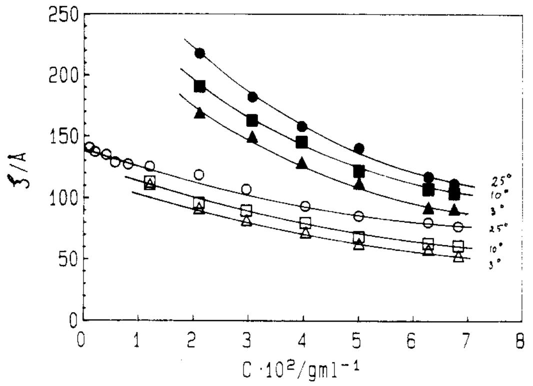

Figure 11. Concentration dependence of the dynamic correlation length (from eq 1) for the permanent gel (filled points) and PVA solutions (open points) at the three temperatures shown.

Permanent Gels of PVA. Figure 10a shows decay time distributions for a PVA gel (C_{PVA} = 5%) at various measurement angles. They consist of a single sharp peak, which is displaced to longer time on the time axis compared to the fast cooperative mode in the PVA solution at the same angle. The relaxation rate is precisely q^2-dependent, i.e., corresponds to a diffusive process, and a homogeneous gel results on cross-linking with glutaraldehyde. At low angle, the base line increases slowly with the gels to a value of about 14% and with the solutions to about 4%. In the estimation of correlation lengths below, correction has been made for heterodyning deriving from the static scatterers causing the base line. A typical autocorrelation function is shown in Figure 10b. In some systems (polyacrylamide gels, for example[14]) a large floating base line (60–80%) has been reported, denoting the presence of static scatterers which are immobile on the time–distance scale of the experiments, and these presumably derive from the method of gel preparation.

Geissler and co-workers[21] have recently discussed the characteristic lengths that are important in describing the microscopic aspect of permanent gels: R_t, the distance between two topologically connected junction points; R_s, the mean distance between nearest spatial neighbor junction points; ξ, the polymer–polymer correlation length analogous to the characteristic dimension defining the semidilute polymer solution.

Perhaps unexpectedly, the dynamic correlation lengths, evaluated from the network mode for gel and solution by using eq 1, are not equal, as shown in Figure 11 for the respective data at different temperatures. At a given concentration, the correlation length in the gel is considerably larger than in the solution; the ratio is about 1.6. A similar difference (a factor of 1.5) has been noted by Geissler et al.[11] who compared the correlation lengths in polyacrylamide solutions and gels by using neutron scattering. This effect may be anticipated when the PVA chains are cross-linked by a bridging mechanism with the glutaraldehyde moieties of fixed length. On the other hand, one might have expected that the dynamic behavior of the chain segments would be essentially unaffected by the presence of the widely separated cross-links. Geissler et al. point out that a contributory cause for the observed reduction in the osmotic pressure of the gel (and hence a longer correlation length) will arise since the cross-links limit the volume available to the polymer chains in the gel. However, since the cross-linking concentration is low (≃1%) in the present case, this volume limitation should not be the source of the observed difference in correlation lengths. The usually made assumption is that polymer gels differ from the un-cross-linked polymer solution at the same concentration only by an additive elastic free energy term. Horkay et al. have shown[39] that this is in general not true; the mixing pressure in the gel has been shown experimentally to be sig-

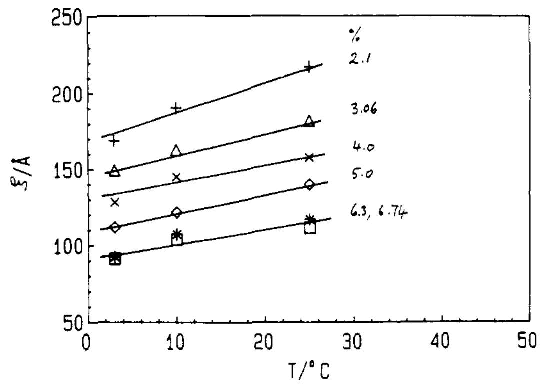

Figure 12. Temperature dependence of the dynamic correlation length for the permanent gel at various concentrations: (+) 2.1%; (△) 3.06%; (×) 4.0%; (◇) 5.0%; (*) 6.3%; (□) 6.74%.

nificantly lower than in the solution, contrary to the usual assumption of their identity. Recent experiments with acetylated PVA gels and solutions[44] show, however, that the relationship between the correlation lengths in the gel and corresponding solution is reversed and therefore at least part of the observed effect may be related to differences in hydrogen bonding.

For the permanent gels at the different temperatures, a log–log plot between the correlation length and concentration gives an average slope of −0.72. This value, approximates that found for very long flexible chains (≈0.68). Since a linear relationship is found in Figure 8, however, the present data do not necessarily support a scaling interpretation. SANS investigations of swollen networks[11] have shown that in a good solvent $\xi \sim C^{-0.75}$ in accordance with scaling predictions for semidilute solutions. At higher concentrations deviations from a simple concentration dependence may be anticipated. Thus Davidson et al.[32] find for polystyrene gels in toluene the predicted scaling law dependence on concentration up to a polymer volume fraction of 0.06, with a sharp deviation at higher C.

PVA gels do not resemble those formed by cross-linking stiff polymer chains such as polysacchrides. Dynamically, the latter gels are almost completely stationary at the molecular level,[37,38] and the measured relaxation rates do not exhibit a simple q^2 dependency. PVA gels typify, instead, those formed from other flexible chains (e.g., polyacrylamide) in which the segments are highly mobile and are characterized by diffusive motion. With polyacrylamide gels, however, the correlation length is very much shorter at a given cross-linking level than those with PVA gels, and gels with a coherent structure are not formed below about 2% cross-linking. The overall picture that emerges is that, unlike semidilute solutions, gels have individual characteristics that not only stem from the polymer–solvent pair but also reflect the cross-linking process and the nature and frequency of the bridges themselves.

Figure 12 shows the temperature dependence of the correlation length for the permanent gel that reflects the cooperative response of the structure to a change in solvent quality. The trend is similar to that in Figure 9 but, at a given temperature and concentration, ξ is larger for the permanent gel than for the solution.

Parts a and b of Figure 13 compare the distributions for the gel at different concentrations with those of the corresponding PVA solutions from which they have been prepared. (In order to give an appraisal over the whole time domain examined, the distributions are shown with a "tight" log scale, and the positions of the gel mode peaks then become insensitive to changes in decay time of the magnitude shown in Figure 11.) In Figure 13b, the slow cluster mode is discernible at concentrations of 2 and 3% but is of low amplitude. At C = 4% and above only a single gel mode peak is present. In the solutions, the relative amplitude of the gel mode is very small, the cluster mode dominating the spectra. There are thus substantial differences in the distributions of solution and gel for this particular system which would not be anticipated in "well-behaved" semidilute systems not exhibiting cluster formation, e.g., polystyrene in toluene. Some experiments were made with a varied concentration of cross-linking agent. Except for the lower cross-linking limit of 0.25% at which the gel structure has not become homogeneous and slow relaxations are still evident, the distributions are exclusively single-peaked as seen in Figure 14a (most of the data in this study refer to gels having a cross-link density of 1% based on the PVA monomer weight, which corresponds to about 20 cross-links per PVA chain). The correlation length of the gel mode initially increases above the value in the solution as the level of the cross-linking agent is raised. Eventually, the correlation length decreases sharply as indicated in Figure 14b. Geissler et al.[11] have made similar observations.

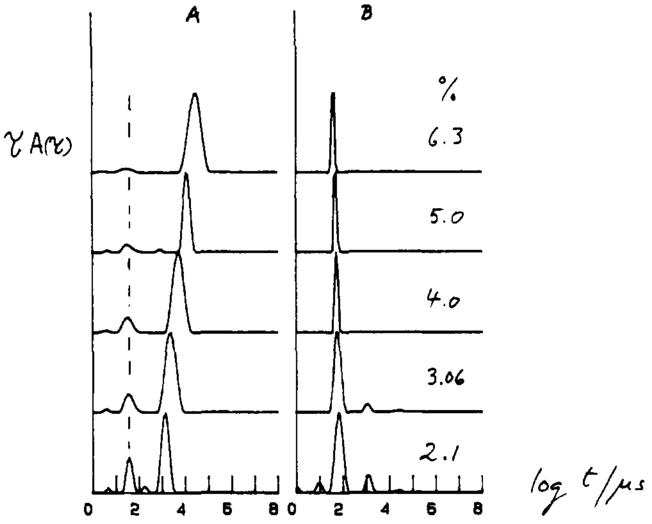

Figure 13. Comparison of decay time distributions for (a) solutions and (b) permanent gels at different concentrations (temperature 25 °C and measurement angle 60°). The approximate position of the transient gel mode in the PVA solutions is indicated by the vertical dotted line.

Figure 15 shows a log–log plot of the longitudinal elastic modulus (M_{os}) versus concentration. M_{os} was obtained from the static light-scattering data as $M_{os} = C(\partial\pi/\partial C) = (KC/R_{\theta=0})RTC$, where R is the gas constant and T the absolute temperature. Theory predicts that the slope of 2.25 should be observed, and this is shown by the broken line. The least-squares mean value of the experimental slope is 2.45. A similar correlation has earlier been established by Geissler and Hecht[40] for water-swollen polyacrylamide gels.

Conclusions

Gels prepared from PVA through cross-linking flexible linear chains of the polymer in solution with glutaraldehyde differ significantly from the semidilute solutions from which they have been prepared, in contrast to earlier reports. The solutions are characterized by the presence of a slow hydrodynamic relaxation in addition to the fast "blob" relaxation describing the network. The former disappears on cross-linking. At a given concentration, the dynamic correlation length for the gel is almost

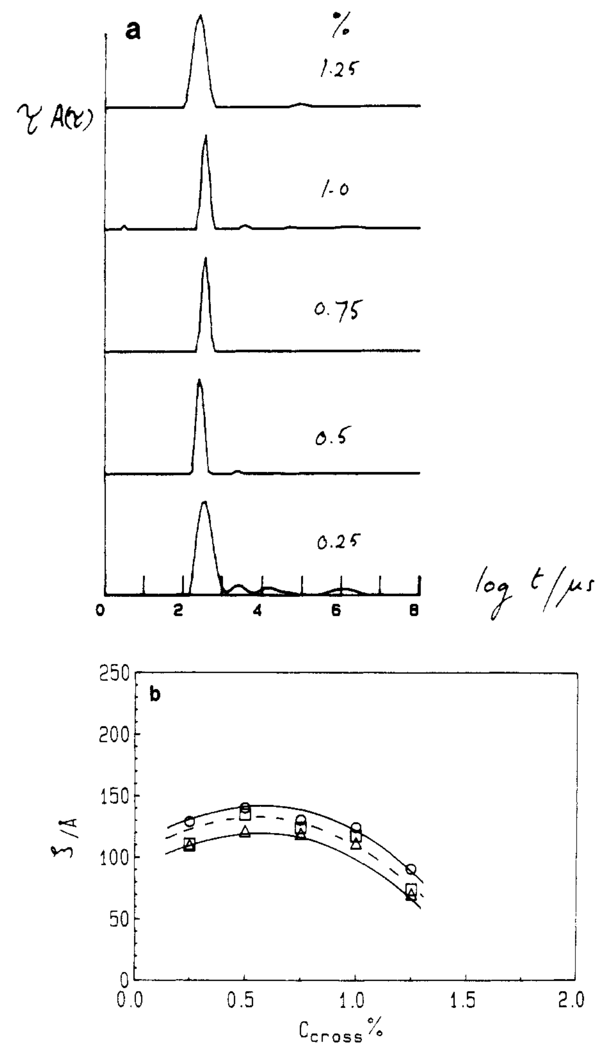

Figure 14. (a) Decay time distributions for the PVA permanent gels at different levels of glutaraldehyde cross-linking. (b) Dynamic correlation length shown as a function of the concentration (%) of cross-linking agent for a 4% PVA gel at 3 °C (△); 10 °C (□); 25 °C (○).

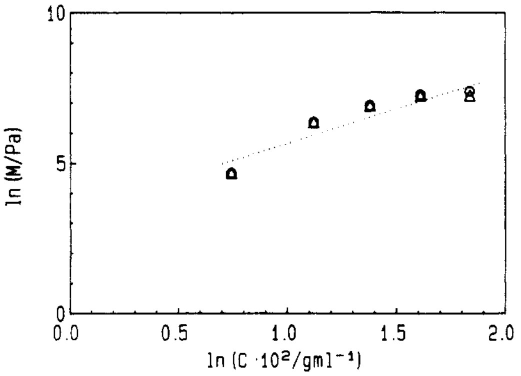

Figure 15. log–log plot of the longitudinal elastic modulus (M_{os}) versus PVA concentration at the temperatures 22 °C (○) and 4 °C (△). The dotted line has the theoretical slope of 2.25.

twice that for the corresponding solution, even though the gels are created by sparse cross-links (≈1% based on the monomer weight).

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