

Dynamic properties of polyacrylamide gels and solutions

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(Received 8 December 1989; revised 19 April 1990; accepted 27 April 1990)

Decay time distributions have been obtained by Laplace inversion of the autocorrelation functions in dynamic light scattering for polyacrylamide (PAA) solutions and gels prepared in an identical manner except for the addition of crosslinking agent. The measurements were made as a function of PAA concentration, crosslinking concentration and temperature. The purpose was to establish the similarities and differences between the gel and the analogous solution and also to examine the connection between these variables and the dynamic behaviour of the gel. While the solutions have a comparatively complicated dynamic structure, the gels are precisely single-exponential at PAA concentrations above about 2%. Over the same concentration range, the solutions have a slowly relaxing component of narrow distribution in addition to the network mode formed through interchain entanglements. The slow mode, which has a strong negative concentration dependence, finally disappears at $C_{\text{PAA}} \approx 10\%$. The dynamic polymer-polymer correlation length (ξ_{H}) for the permanent gel, which is considerably larger than that for the corresponding solution, is weakly dependent on concentration ($\xi_{\text{H}} \sim C^{-0.22}$ for both gels and semidilute solutions) and is independent of the temperature. ξ_{H} increases with increasing concentration of bisacrylamide C_{bis} , reaching a plateau in the vicinity of $C_{\text{bis}} = 5\%$. The static screening length takes the same value in solutions and gels and is dependent on concentration: $\xi_{\text{s}} \sim C^{-0.65}$. The two correlation lengths become approximately equal at high crosslinking density. The longitudinal elastic modulus (M_{os}), evaluated from static light-scattering data, shows the theoretically expected dependence on PAA concentration.

(Keywords: gels; solutions; light scattering; correlation length)

INTRODUCTION

There is an extensive literature on polyacrylamide (PAA) gels (for example, refs. 1–15), which stems from their ready preparation and diverse applications as separation media. Particular interest has thus been paid to the transport of particles within these gels^{10–14}. As regards the structure and properties of the gels themselves, dynamic light scattering (DLS) and small-angle neutron scattering (SANS)¹⁵ are particularly convenient ways of probing the static and dynamic behaviour since the space and time resolution are of the required order. Previous studies described in the literature have evaluated the DLS data using either a forced fit to a single-exponential function or else the method of cumulants. However, with the advent of multi-tau (broad-band) autocorrelators and also the simultaneous development of several modified methods of performing Laplace inversion on the data of wide timescale (e.g. CONTIN¹⁶, the maximum entropy method, MAXENT¹⁷, REPES¹⁸, etc.), one now has access to the ‘complete’ (that is to say, within the resolving power of the light-scattering method) distribution of decay times for complex systems. It should be added, however, that extraordinary precautions are

required to minimize the inclusion of spurious peaks and it is necessary to assemble data of unusual statistical precision to ensure this. Recent communications^{19,20} have discussed this aspect. Thus, in principle, the elucidation of solution and gel dynamics should be more straightforward than hitherto. This communication describes measurements on water-swollen polyacrylamide (PAA) gels and the influence of concentration, temperature and crosslinking density. Comparison is made with the corresponding solution (i.e. the identically prepared system but in the absence of added bisacrylamide). A recent paper²¹ dealt with a similar system (poly(vinyl alcohol) (PVA) gels and solutions) but where the gels had been formed by crosslinking the essentially monodisperse chains using glutaraldehyde. Significant differences may be expected between these gels and those formed starting with the monomer as with PAA gels.

Earlier studies of permanent gels in which the chains are connected by chemical crosslinks and entangled semidilute solutions where the chains interact through transient junctions have provided a measure of support for their similarities, where scaling laws have provided the basis for the comparison. One would anticipate differences only at very long times, i.e. much greater than the disentanglement time in solution. More recently, however, it has become clear that the polymer-polymer correlation length is substantially greater in the gel.

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0032-3861/90/101960-08

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EXPERIMENTAL

Preparation of polyacrylamide gels and solutions

Gels were prepared using standard procedures (e.g. ref. 5), using synthesis-grade acrylamide and *N,N*-methylene-bisacrylamide from Merck, FRG. As an example of the relative quantities of reagents used, the following amounts were employed for the $C_{\text{PAA}} = 5\%$ w/w gel having 2.5% w/w bisacrylamide (based on acrylamide plus bisacrylamide): 2.45 ml 10 wt% acrylamide, 1.0 ml 0.5 wt% bisacrylamide, 1.35 ml water, 0.1 ml 1 wt% ammonium persulphate and 4 μl tetramethylethylenediamine (TEMED). With different acrylamide concentrations, the quantities of persulphate and TEMED were adjusted proportionately. Prior to addition of initiator, the solutions were degassed under reduced pressure and flushed with nitrogen, filtered through 0.22 μm Millipore filters and allowed to stand for 1 h in crushed ice. No salt or buffer was present and the ionic strength was close to zero. PAA solutions were prepared under precisely parallel conditions, except that no bisacrylamide was added. The samples were prepared directly in 10 ml cylindrical light-scattering cells, flushed with dry nitrogen and sealed. In order to avoid damage to the gels, the lowest temperature used in measurements was 3°C. Hecht and Geissler⁹ note that PAA gels freeze at -7.5°C . The gels are not, however, stable to repeated heating and cooling; there is very slow, irreversible contraction with such 'annealing'.

Dynamic light scattering

DLS measurements were made using the apparatus and technique described earlier^{22,23}. The laser was a 35 mW He-Ne (633 nm) Spectra Physics model. The autocorrelator was a multi-tau model ALV-3000 from ALV-Langen, FRG, allowing 23 simultaneous sampling times and thus a monitoring of very widely spaced decays (up to nine decades in time) in the same experiment. Laplace inversion, to obtain the distribution of decay times, was made using REPES¹⁸, which directly minimizes the sum of the squared differences between the experimental and calculated autocorrelation functions $g^2(t)$ using non-linear programming. With data of low noise, REPES can handle data of unusual decay time width without giving spurious peaks. The 'smoothing' parameter P (probability to reject)—which takes values from 0 to 1, corresponding to zero and complete smoothing—was given the value 0.5. In each solution, the moments of the peaks are given in the output, yielding the relative amplitude and frequency of each resolved component. The distributions were found to be closely similar to those obtained using, for example, CONTIN¹⁶ and the maximum entropy method, MAXENT¹⁷. It is important that the gels prepared as above contained no static heterogeneities. Thus measurements could be made in the homodyne mode and no significant baseline was observed in the correlation functions (see, for example, Figure 1).

Static light scattering

Intensity light-scattering measurements were made using a photon-counting device supplied by Hamamatsu. The light source was a 3 mW He-Ne laser (633 nm). The optical constant for vertically polarized light is $K = 4\pi n_0^2(\text{dn}/\text{dC})^2/N_A \lambda^4$, where n_0 is the solvent refractive index and dn/dC the refractive index increment

($=0.149 \text{ ml g}^{-1}$ at 25°C^{24}). The reduced scattering intensity, KC/R_θ , was measured on the same solutions and gels as used for dynamic light scattering. R_θ is the Rayleigh ratio obtained by calibration measurements with benzene: $R_{90} = 8.51 \times 10^{-6}$ at 25°C^{25} . There was no significant angular dependence of KC/R_θ in the range 45° to 135° for either gels or solutions. All measurements were made in concentration ranges in which multiple scattering effects could be neglected. Since the gels contained negligible heterogeneities, the longitudinal elastic modulus, M_{os} , could be evaluated directly from $M_{\text{os}} = (KC/R_{90})RTC$, where R is the gas constant and T the absolute temperature.

RESULTS AND DISCUSSION

Figure 1 depicts typical time correlation functions collected over about seven decades on the timescale in a single experiment for a gel (a) and solution (c) together with the corresponding decay time distributions obtained by Laplace inversion using the REPES routine. While the gel is typically single-exponential, the solution is approximately bimodal.

Decay time distributions for gels and solutions

Figure 2a compares decay time distributions for gels (crosslinking 2.5%) with solutions having the same nominal PAA concentration in the range 2% to 10% and Figure 2b shows the angular dependence of the distributions for the gel $C_{\text{PAA}} = 7.5\%$ with a crosslinking degree of 2.5%.

The distributions shown in Figure 2a for the gels have a much more simple character than the corresponding solutions. At concentrations at and above 2.5% the decay time distributions show essentially only the q^2 -dependent gel mode (see, for example, Figure 5, below). The uniformity of the gels at concentrations greater than 2.5% is interesting in light of recent attention paid to inhomogeneities in lightly crosslinked polyacrylamide gels. With low levels of bisacrylamide (0.1–0.5%), Hecht *et al.*²⁶ and Mallam *et al.*²⁷ showed that such gels contain extensive regions which are characterized by the same correlation length but that there are also structural heterogeneities having a length scale in the range 50–2500 Å.

Figure 3a depicts the influence of the crosslinking level on the uniformity of gel structure at a fixed PAA concentration of 2.5%. Already with only 0.5% bisacrylamide there is an almost complete domination of the distribution by the diffusive gel mode. At the higher levels of C_{bis} , only the gel mode is present. Figure 3b shows the role of C_{bis} with the concentration of polyacrylamide $C_{\text{PAA}} = 2\%$ from a low-angle measurement. Slow modes are present at all levels of C_{bis} . These distributions have been obtained by fitting to the sum of a Gaussian peak and a generalized exponential function as described in ref. 20. It may be noted, however, that below a PAA concentration of about 2%, stable, uniform, gels are not formed and a 1% 'gel', for example, is still in the 'pre-gel' state. Although the relaxation mode for the gel is well developed at $C_{\text{PAA}} = 1\%$, and represents a significant portion of the total scattering intensity, the structure of the suspension is not yet uniform and slower modes are also displayed. Figure 3c shows a 1% gel at high angle at which the slow modes are of low relative intensity.

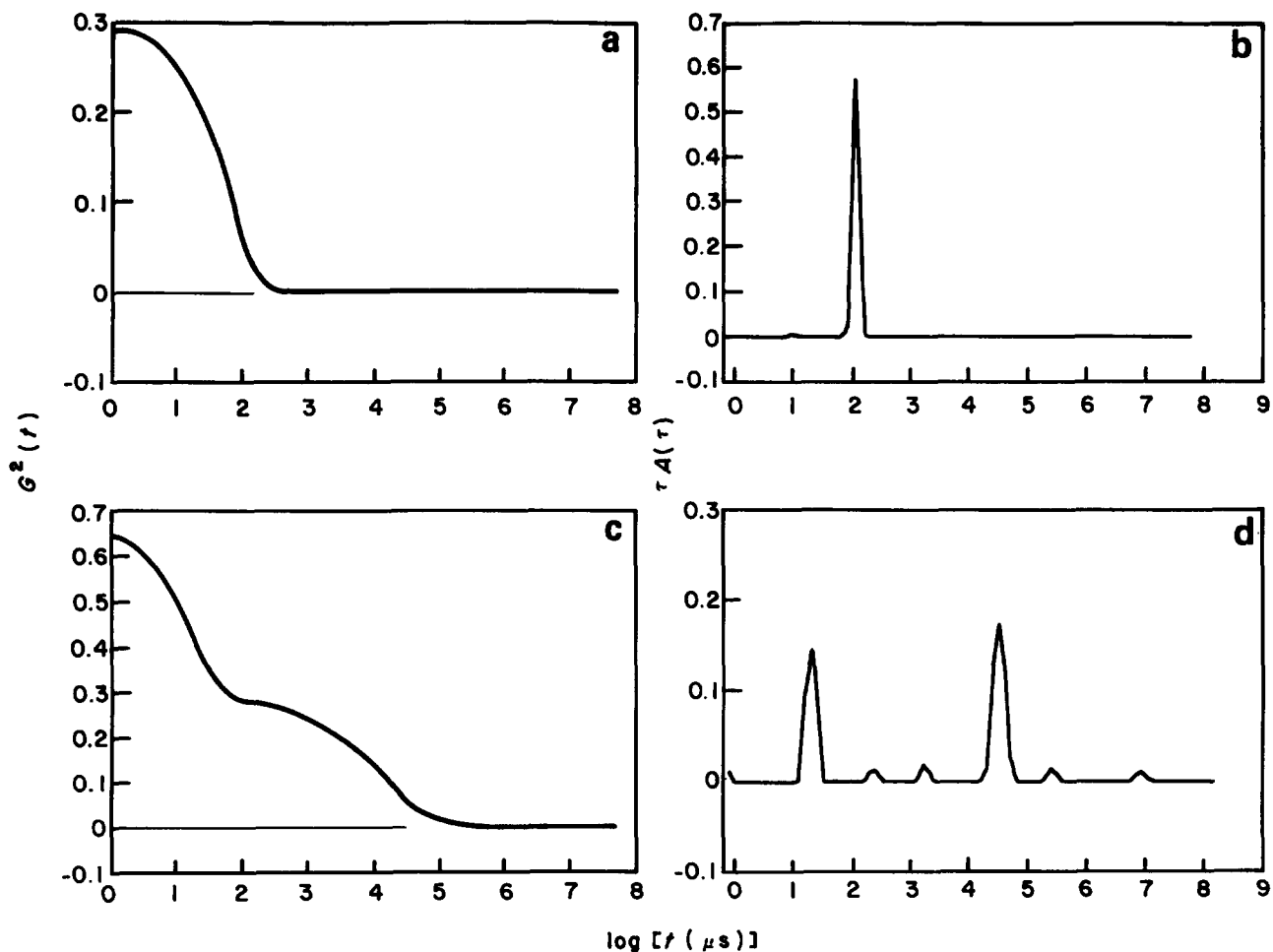


Figure 1 Autocorrelation functions from dynamic light scattering (a, c) and the corresponding decay time distributions obtained by Laplace inversion (b, d). (a, b) Polyacrylamide gel ($C_{PAA}=5\%$); crosslinking density 2.5% ($\theta=60^\circ$; $25^\circ C$). (c, d) Polyacrylamide solution ($C_{PAA}=7.5\%$) ($\theta=90^\circ$; $25^\circ C$)

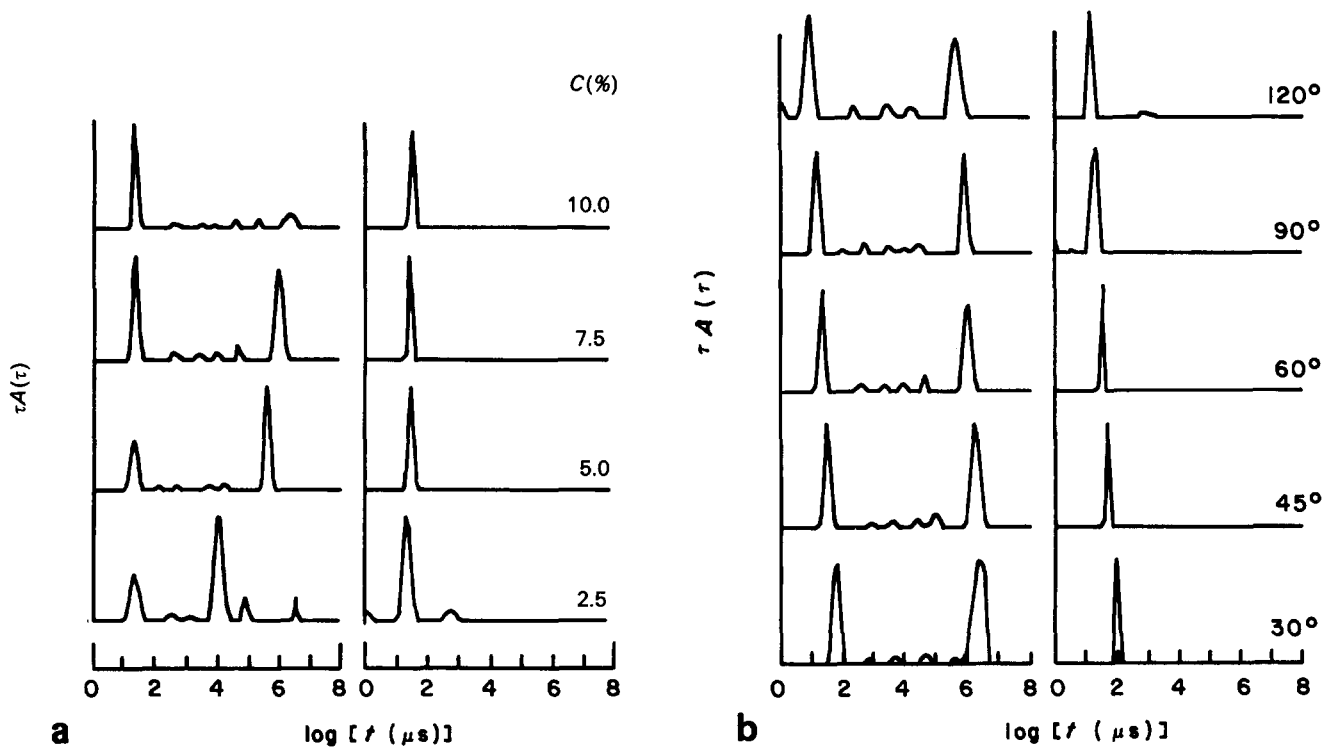


Figure 2 (a) Comparison of decay time distributions for polyacrylamide solutions (left) and gels ($C_{bis}=2.5\%$) (right). Data obtained by Laplace inversion of DLS autocorrelation curves measured at $\theta=60^\circ$ and $25^\circ C$. The fastest peaks correspond to the network mode.

(b) Angular dependence of decay time distributions, as under (a), for solution and gel ($C_{bis}=2.5\%$) with $C_{PAA}=7.5\%$ at $25^\circ C$. The various modes are all approximately q^2 -dependent (see also Figure 5)

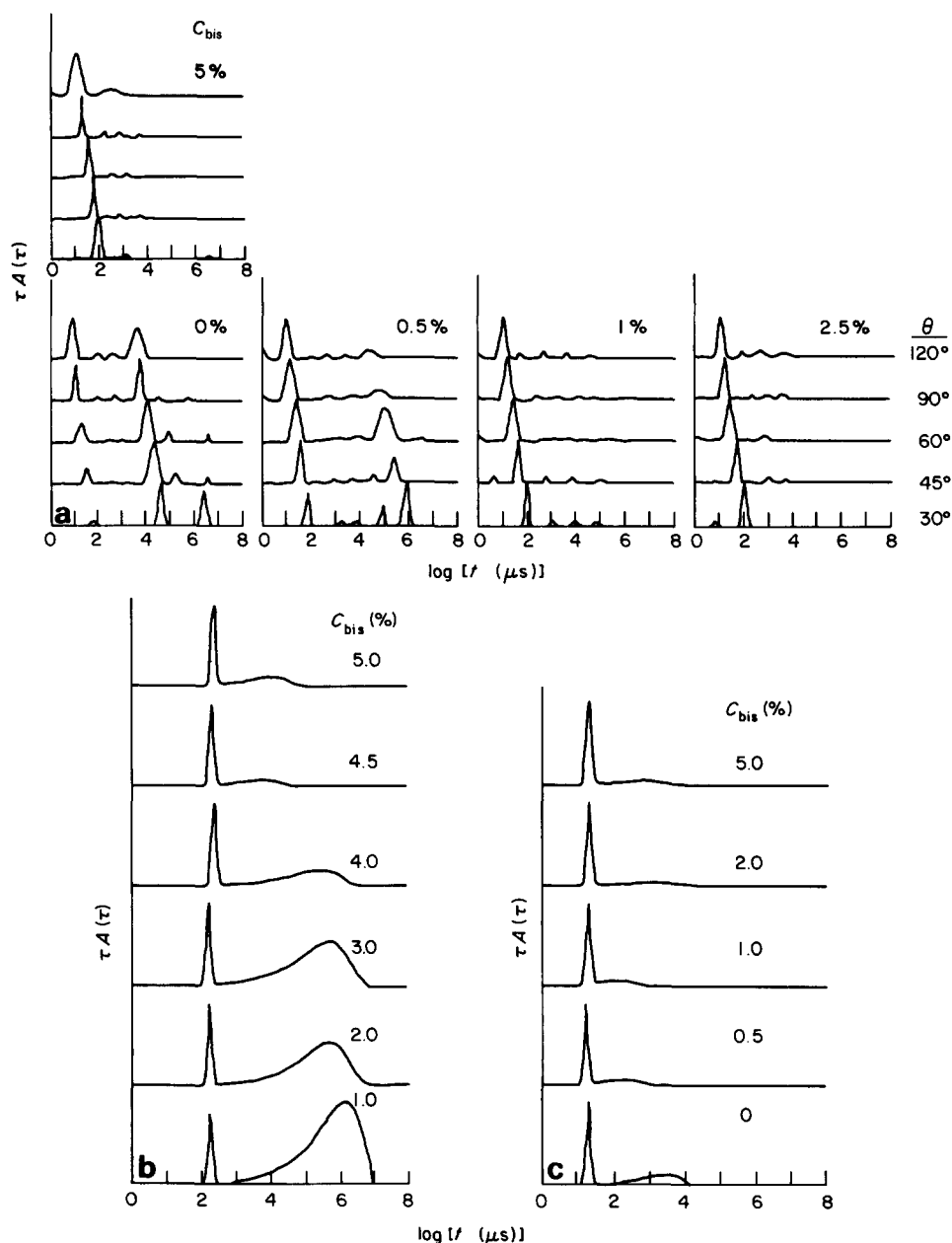


Figure 3 (a) Decay time distributions for the $C_{PAA} = 2.5\%$ gel with different levels of crosslinking agent as shown at 25°C. The measurement angle is indicated. (b) Decay time distributions for the $C_{PAA} = 2\%$ gel at different levels of crosslinking. Measurement angle = 30° and temperature 25°C. (c) As for (b) but with $C_{PAA} = 1\%$. Measurement angle = 120° and temperature 25°C. In (b) and (c) the decay time distributions are made by fitting the data to the sum of Gaussian and generalized exponential sum (GEX) as described in ref. 20

Polyacrylamide solutions

The solutions show complicated decay time distributions (Figure 2a): there are several peaks at 2.5%, two main peaks at 5% and 7.5% and essentially a single peak at $C_{PAA} = 10\%$. It may be summarized that, at all concentrations, the peak having the shortest relaxation time corresponds to the gel mode formed by interchain entanglements, and this is anticipated in semidilute solutions. As shown below, the fastest mode is q^2 -dependent (see also Figure 5b) (i.e. it is diffusive) and has a relaxation time that becomes shorter with increasing concentration; Figure 4a. The slower modes, on the other hand, are not typical of semidilute solutions in thermodynamically good, non-aqueous, solvents, although they are frequently found in aqueous solution.

Other water-soluble polymers, such as poly(ethylene oxide)²², polyvinylpyrrolidone²⁸, poly(methacrylic acid)²⁹ and the recently studied poly(vinyl alcohol)²¹, reveal the presence of one or more 'slow' modes. The latter are diffusive and show a pronounced negative concentration dependence as shown in Figure 4a, which may be attributed to the growth of clusters or groups of chains moving as hydrodynamic entities. The latter frequently grow in size with increasing concentration, but are not temperature labile. The different diffusive modes are observable in the light-scattering experiment as a consequence of the size polydispersity in the system. As shown by Phillis³⁰ and Pusey *et al.*³¹ for hard spheres and by Benmouna *et al.*³² for linear chains and copolymers, in the case of bidisperse systems the signal

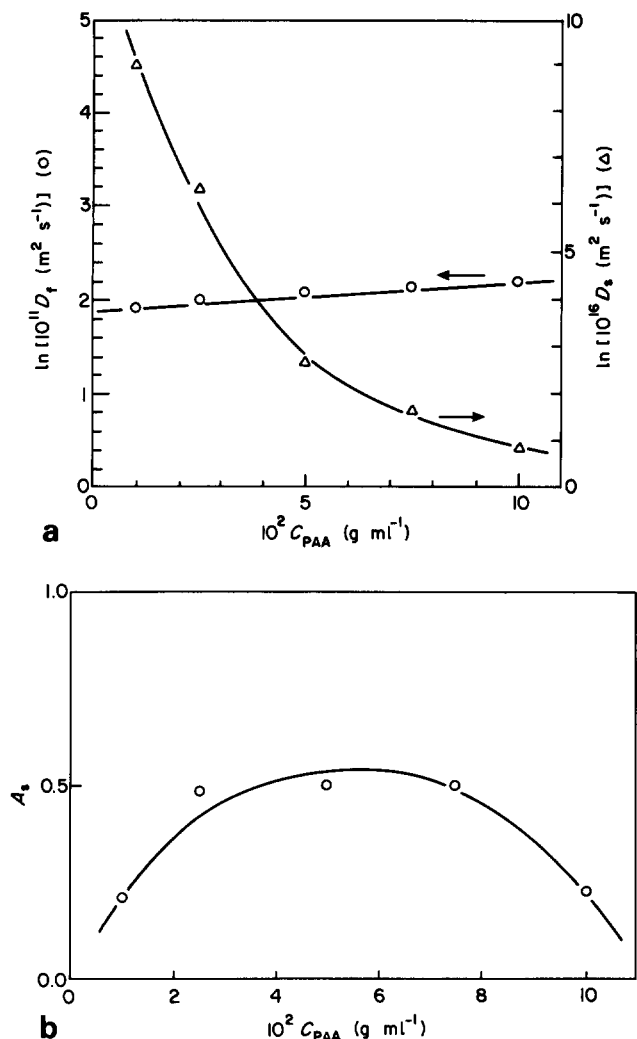


Figure 4 (a) Semi-logarithmic plot of the gel mode (D_t) and the main slow mode (D_s) in PAA solutions at 25°C. Log-log plots give exponents of 0.22 (D_t) and -3.7 (D_s). (b) Relative amplitude of the slow mode as a function of PAA solution concentration

from one species will be modulated by the second, leading to a bimodal autocorrelation function. (It is not necessary that one of the species is matched in refractive index to the solvent.) The two relaxation rates correspond to the collective diffusion coefficient (D_C) on the one hand and the interdiffusion coefficient (D_I) on the other. At a suitably low concentration of a minor component one obtains the self-diffusion coefficient. We have recently demonstrated³³ that precise measurements of the self-diffusion coefficient may be made in this way in homopolymeric mixtures of two molecular weights. One may conclude that in the present case the slower peak approximates the self-diffusion of variously sized clusters or ordered domains. The slope of a log-log plot of D_s versus C corresponds to $D_s \sim C^{-3.7}$. This slope is much greater than anticipated for the self-diffusion of a single, flexible chain in a semidilute solution (-1.75 in a thermodynamically good solvent³⁴). However, it follows the trend now established for self-diffusion in congested systems, where it is experimentally observed that the exponent decreases monotonically with increasing 'matrix' concentration and may take values in excess of -3 .

Figure 4b shows the relative intensity of the slow mode

for PAA semidilute solutions of increasing concentration. With the recently examined²¹ poly(vinyl alcohol) solutions, the decay time distributions were essentially bimodal, the fast component corresponding to the transient network and the slow to clusters, or groups of chains. At higher concentrations, the cluster peak dominated the distribution completely. In the polyacrylamide solutions, on the other hand, there is a paucidisperse mixture of different discrete components, but at 10% the transient gel component is dominant¹. The polyacrylamide coils behave in a similar manner and form a homogeneous network at higher concentrations.

Dynamic and static correlation lengths

There are two physically different screening lengths that are important in semidilute solutions and gels. One is the screening length for the hydrodynamic interactions between polymer segments (ξ_H), which is defined in terms of the fast cooperative diffusion mode measurable in, for example, DLS experiments:

$$\xi_H = kT / 6\pi\eta_0 D_t \tag{1}$$

where η_0 is the solvent viscosity and kT the energy term. The other is the screening length for the excluded-volume interactions (ξ_s), which determines the thermodynamic properties of the system. Geissler *et al.*³⁵ have formulated other length scales that are important in describing gel structure: these are the end-to-end distance of a given coil (R_t)—i.e. the distance between the topologically

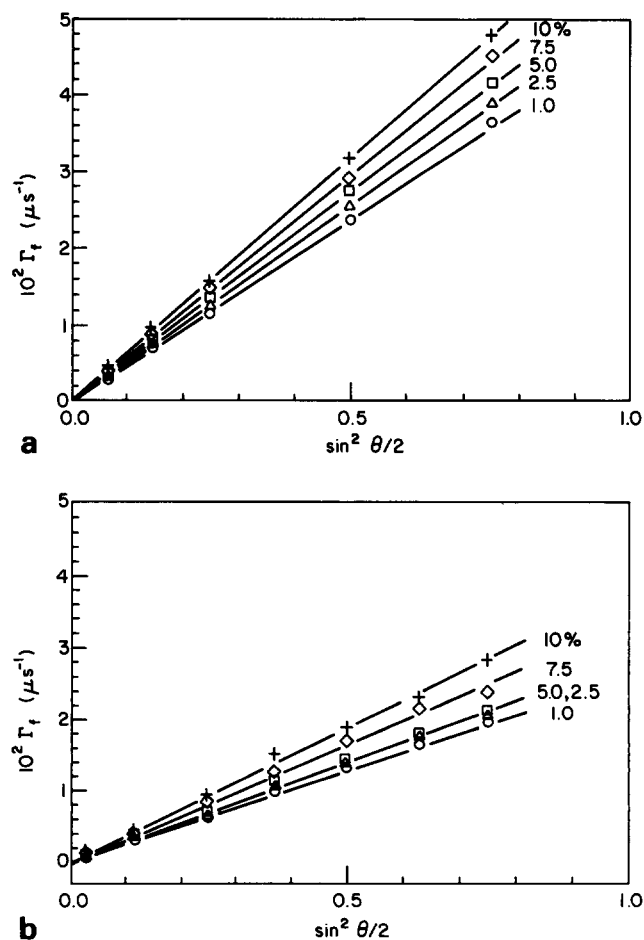


Figure 5 Relaxation frequencies (Γ) for the fastest component in the decay time distributions: (a) PAA solutions; (b) gels with $C_{bis} = 2.5\%$

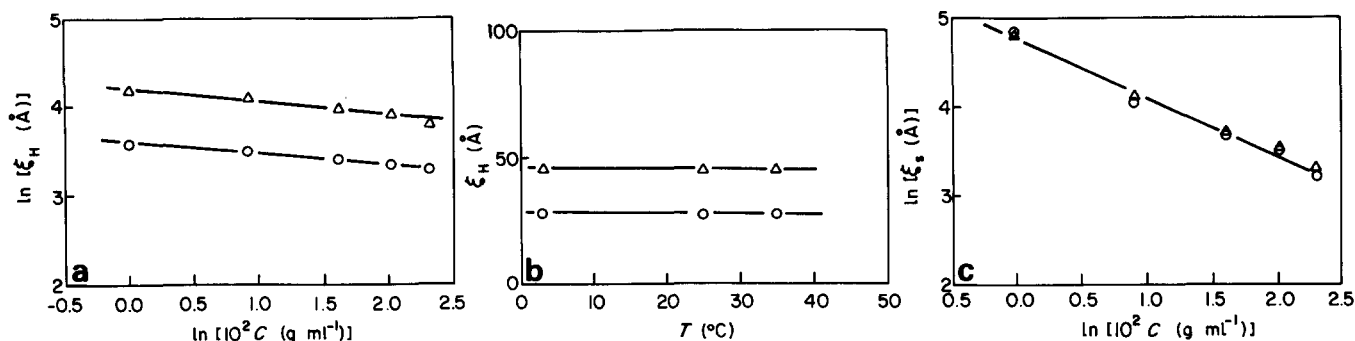


Figure 6 (a) Concentration dependence of the dynamic polymer–polymer correlation length for polyacrylamide solutions (O) and gels with $C_{\text{bis}}=2.5\%$ (Δ). (b) Dynamic correlation length as a function of temperature for PAA gels with $C_{\text{bis}}=2.5\%$ (Δ) and solutions (O), both with $C_{\text{PAA}}=10\%$ w/v. (c) Analogous plot to (a), but for the static correlation length evaluated from intensity light-scattering data using equation (2) for solutions (O) and gels (Δ)

connected junctions—and the distance between spatially neighbouring junction points (R_s). These various parameters vary characteristically and differently with the volume fractions of chains present. Since we concentrate here on the gel/solution comparison, the polymer–polymer correlation lengths are the quantities of immediate relevance to our discussion.

Figure 6a compares ξ_H for solutions and gels as a function of PAA concentration. The ratio ($\xi_{\text{solution}}/\xi_{\text{gel}}$) changes from about 1.9 at $C=1\%$ to 1.7 at $C=10\%$. A similar ratio was found by Geissler *et al.* using neutron scattering⁷ and was also reported for the PVA gels²¹. ξ_H is approximately temperature-independent (Figure 6b), a behaviour that contrasts with that of PVA gels, which exhibit a decrease in ξ_H towards lower temperatures for which the solvent quality improves. There is a small decrease in ξ_H over the concentration range used. The latter corresponds to $\xi_H \sim C^{-0.22}$, which is a much smaller exponent than predicted (-0.75 ³⁴) for the dependence of flexible chains on concentration in semidilute solutions. (We note here that the gel mode diffusion coefficients have been corrected for solvent backflow by division with $(1-\phi)$, where ϕ is the polymer volume fraction given by $\phi = \bar{v}_2 C$, with \bar{v}_2 the partial specific volume and C the concentration.) This correction is very small in the present concentration range. It is important that the same exponent is observed in both the semidilute solutions and the gels, and thus is independent of possible gel heterogeneity³.

This inconsistency between the observed and predicted exponents may be explained by the concentration dependence of the true chain friction in the PAA solutions and gels, which has been found to differ from the water viscosity^{2,3,9}. The actual friction is higher than the latter and depends on the hydrodynamic structure of the network². Figure 6c shows the static correlation length (ξ_s) plotted as a function of concentration in a log–log diagram, where ξ_s was evaluated from the intensity light-scattering data using the relationship given by Geissler *et al.*⁷:

$$M_{\text{os}} = 3kT/4\pi\xi^3 \quad (2)$$

and M_{os} is the longitudinal elastic modulus, $M_{\text{os}} = C(\partial\pi/\partial C)$. The numerical values of ξ_s obtained in this way from light-scattering intensity measurements were observed to agree well with those obtained by elastic neutron scattering on polyacrylamide gels. In the present system, ξ_s for both solution and gel are

experimentally indistinguishable and the line is described by: $\xi_s \sim C^{-0.65}$. We note that Mallam *et al.*²⁷ found a similar agreement between correlation lengths determined by different methods. This exponent contrasts⁴ with the very low exponent (-0.22) observed in Figure 6a for the dynamic correlation length. This, as mentioned above, is probably a consequence of a concentration dependence of the polymer friction. We note that Hecht and Geissler¹⁴ reported an exponent of 0.65, and Sellen³⁶ found 0.63, for the concentration dependence of the cooperative diffusion coefficient. A possible explanation of this inconsistency between the values may be found in the different preparation procedures for the gels.

The diffusion data from several sources depicted in Figure 7a show that, apart from the scattering in the absolute values of D_f , e.g. the early data of Tanaka², the differences in the dependence of D_f on PAA concentration are not striking. Part of the observed variation in absolute values of D_f may arise from changes in the gel itself, after crosslinking. Thus we have observed that, when PAA gels are subjected to temperature cycles over periods of several months, there is an irreversible contraction of the structure, presumably into more compact arrangements of the chains favouring intramolecular hydrogen bonding.

Figure 7b depicts the temperature dependence of the cooperative diffusion coefficient in this and other investigations. The trend is similar but with a significant variation between the values of D_f at any given temperature. This is, as mentioned above, probably a consequence of differing preparation procedures/treatments of the gels. The crosslinking density has a significant effect on the polymer–solvent interactions in very dilute gels as shown in Figure 8a. In the region where stable gels are formed ($C_{\text{PAA}} > 2\%$) there is a very modest change in ξ_H . Figure 8b displays data for the influence of the crosslinking density on ξ_H for a constant polymer concentration of 5% at various temperatures. Figure 8c compares the dynamic and static correlation lengths as a function of C_{bis} . At the higher crosslinking levels, these two length scales become approximately equal.

Figure 9a shows the longitudinal elastic modulus ($M_{\text{os}} = C \partial\pi/\partial C$) as a function of concentration in a log–log diagram. M_{os} has been derived from the static light-scattering data (see ‘Experimental’). The dotted line through the data is drawn with the theoretically expected slope of 2.25 (since the osmotic pressure of a gel or

solution in a good solvent is given by $\pi \sim C^{2.25}$ (ref. 34)). A similar correlation has been observed by Geissler and Hecht^{5,6} from the results of neutron scattering and quasielastic light scattering on polyacrylamide gels. Our present results agree numerically with the values given by Geissler *et al.*³⁷ also using a light-scattering method.

Figure 9b shows the temperature dependence of the elastic modulus. This result shows that the static correlation length is temperature-dependent, which stands in contrast to the temperature independence of the dynamic quantity in Figure 6b.

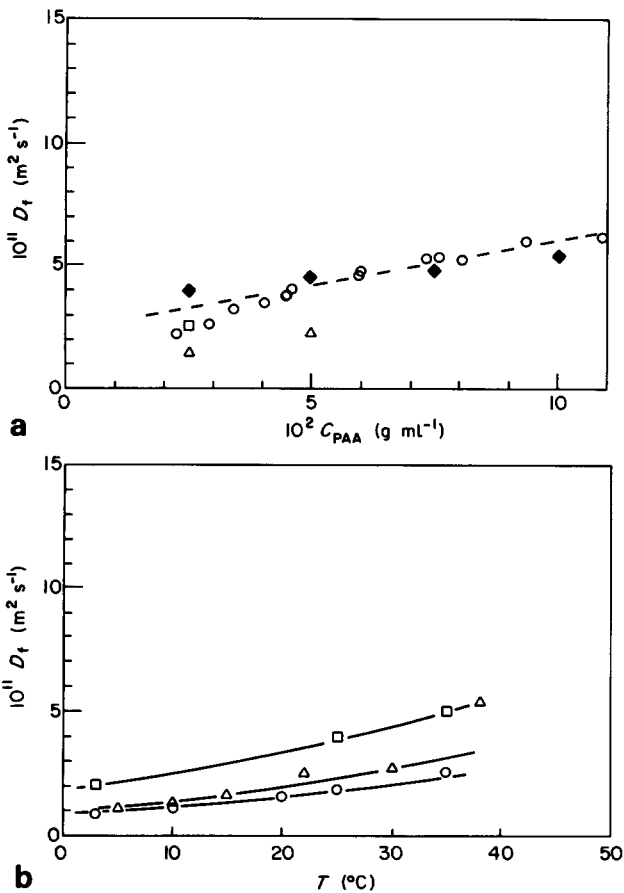


Figure 7 (a) Polyacrylamide gel diffusion coefficients ($C_{\text{bis}}=2.5\%$) from various sources: Hecht and Geissler (O); Tanaka (Δ); Koňák (\square); present work (\blacklozenge). (b) Temperature dependence of gel diffusion coefficients: Tanaka (O); Koňák (Δ); present work (\square)

ACKNOWLEDGEMENTS

Financial assistance from the Bo Rydin Fund (SCA, Sundsvall, Sweden) is gratefully acknowledged. We would also like to thank the Swedish Board for Technical Development (STU) for support of this project. Göran Svensk is thanked for his assistance during the experiments. We are grateful to Drs S. W. Provencher and J. Jakeš for allowing use of their Laplace inversion programs.

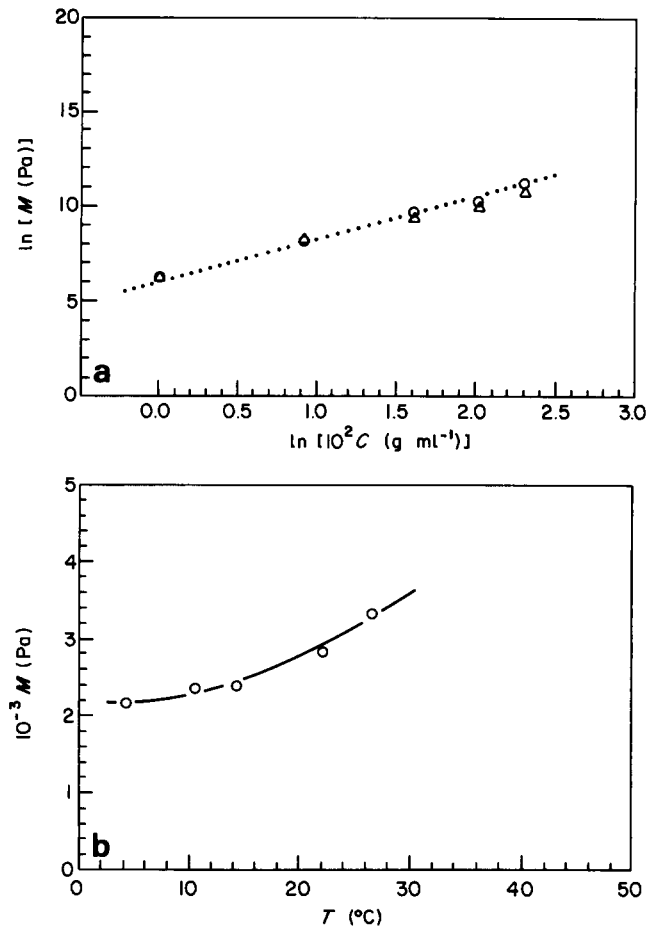


Figure 9 (a) Log-log plot of longitudinal elastic modulus (M_{0s}) versus PAA concentration for solutions (O) and gels (Δ). The dotted line indicates the theoretical slope=2.25. Data are for the PAA gel with $C_{\text{bis}}=2.5\%$ and a temperature of 25°C . (b) Longitudinal elastic modulus (M_{0s}) for the polyacrylamide gel as a function of temperature ($C_{\text{bis}}=2.5\%$; $C_{\text{PAA}}=2.5\%$)

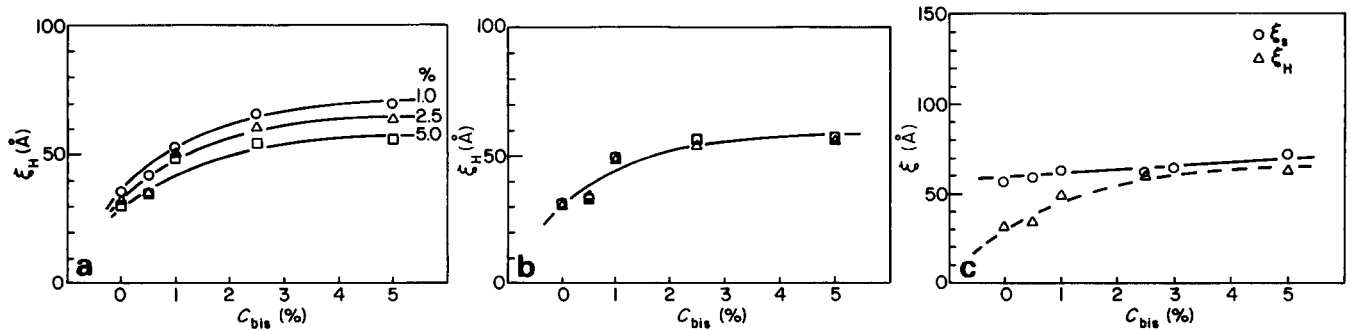


Figure 8 (a) Effect of crosslinking concentration on the dynamic correlation length for gels with different PAA concentrations at 25°C as shown. (b) Dependence of the dynamic correlation length on crosslinking concentration, C_{bis} , for $C_{\text{PAA}}=5\%$, at different temperatures. (c) Variation of static (ξ_s) and dynamic (ξ_H) correlation lengths with the extent of crosslinking of PAA gels with $C_{\text{PAA}}=2.5\%$; temperature 25°C

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