Dynamic Behavior in Poly(vinyl acetate) Gels and Solutions

Wyn Brown* and Liqi Fang

Institute of Physical Chemistry, Box 532, University of Uppsala, 751 21 Uppsala, Sweden

Petr Štěpánek

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia

Received October 12, 1990; Revised Manuscript Received December 4, 1990

ABSTRACT: Relaxation time distributions from dynamic light scattering measurements on poly(vinyl acetate) solutions and gels prepared by acetylation of PVA polymer and gels are reported. The solvents are acetone and methanol (Θ-solvent at 6 °C). In all cases, the gels display sharply unimodal autocorrelation curves. It is significant that the slow (probably viscoelastic) modes observed in semidilute Θ-solutions of high molecular weight chains are not observed in the gels. All gels contain significant proportions of static scatterers. Behavior in acetone solutions is more complex: with lower solvent quality at 6 °C, the correlation curves for the solutions become bimodal due to the presence of clusters. However, at Θ-conditions in methanol solutions the distributions are essentially unimodal. At a given concentration, the dynamic correlation length (ξ_H) in the solution exceeds that for the corresponding gel. The ξ_H-concentration exponents for solutions and gels are closely similar. Below the Θ-temperature in methanol, interchain association leads to large aggregates in the solution that is inhibited by cross-linking in the corresponding gel.

Introduction

A previous paper described relaxation time distributions for PVA gels and solutions in an aqueous medium.[1] PVA is readily acetylated to form the fully derivatized material (denoted PVAc), thereby becoming soluble (swellable) in organic solvents. PVAc gels have been subjected to extensive study in recent years.[2-6] Two solvents were selected: a thermodynamically good solvent, acetone, and a Θ-solvent for PVAc, methanol, at 6 °C.

We wished to examine the relaxation characteristics in organic systems for several reasons. Water-soluble polymers frequently display markedly different solution properties from their organic solvent soluble counterparts owing to the pronounced effects of hydrogen bonding in water which favor certain conformations. In addition, in aqueous systems, clusters of chains are an almost ubiquitous phenomenon in both dilute and semidilute solutions, an aspect which has been described in previous papers.[7-11]

Geissler et al.[12] made the unexpected observation in light and neutron scattering studies on polyacrylamide gels and solutions that the dynamic correlation length in the gel is almost twice that characterizing the transient network in the corresponding semidilute solution of the same concentration. This observation was substantiated in ref 1 for the PVA gels and solutions. It is presumably related to a greater freedom for the chain to adopt more flexible conformations when not cross-linked and is probably related to more extensive hydrogen bonding in this case. It was therefore of interest to make comparison with the fully acetylated material. We note that in earlier measurements Candau et al.[13] found for polystyrene gels in benzene that $\xi_{gel} \approx \xi_{solution}$.

Experimental Section

Gels of PVA were prepared as previously described[1] from the polymer (M_w = 115 000) obtained from BDH chemicals, by cross-linking in aqueous solution using glutaraldehyde at pH 1.5. In the present case a cross-linking degree of 1% was used, where this quantity refers to the number of moles of glutaraldehyde to the PVA monomer.

Acetylation of PVA polymer: PVA was dissolved in the acetylation mixture: 50% v/v pyridine, 40% v/v acetic anhydride, and 10% v/v acetic acid. The reaction was allowed to proceed under reflux at 90 °C for 8 h. Thereafter the PVAc was precipitated by pouring the reaction mixture into cold water. The precipitate was dissolved in acetone and precipitated with water, this step being repeated six times. The residue was washed with water until all pyridine had been removed. Finally the PVAc was dissolved in benzene and freeze-dried to produce a fluffy white powder.

The intrinsic viscosity was determined to be 0.75 dL g^{-1} in acetone at 25 °C and 0.55 dL g^{-1} in methanol at both 25 and 6 °C.

PVA gels were acetylated using the technique described in detail by Horkay and Zrinyl.[5] The previously studied PVA gels[1] were removed from the ampules and treated using fresh acetylating mixture at 90 °C renewed each hour during 8 h. On completion of the reaction, the reaction mixture was replaced by acetone. Thereafter, repeated solvent exchanges to remove all soluble components were performed over a period of 3 months. The gels were equilibrated in the respective solvents, acetone and methanol, and finally sealed into ampules of appropriate diameter. Stoichiometric acetylation was established. The glass-clear gels could be completely dried down and reswollen to the original volume in excess solvent.

Dynamic light scattering measurements were made by using the apparatus and technique described earlier.[14] The laser was a 35-mW He–Ne (633 nm) Spectra Physics model. The autocorrelator was a multi-τ ALV-3000 model from ALV-Langen, FRG, allowing 23 simultaneous sampling times and thus a monitoring of very widely spaced decays (up to 9 decades in time) in the same experiment. Laplace inversion, to obtain the distribution of relaxation times, was made by using REPES,[15] which directly minimizes the sum of the squared differences between the experimental and calculated intensity-intensity autocorrelation function $g^2(t)$ using nonlinear 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 unity, corresponding to zero and complete smoothing, was given the value 0.5. In each solution, the moments of the peaks are provided 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, CONTIN.[16] Measurements were made over the angular range 30–120° in the homodyne mode.

Static light scattering: Intensity light scattering measurements were made by 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 =

0024-9297/91/2224-3201$02.50/0

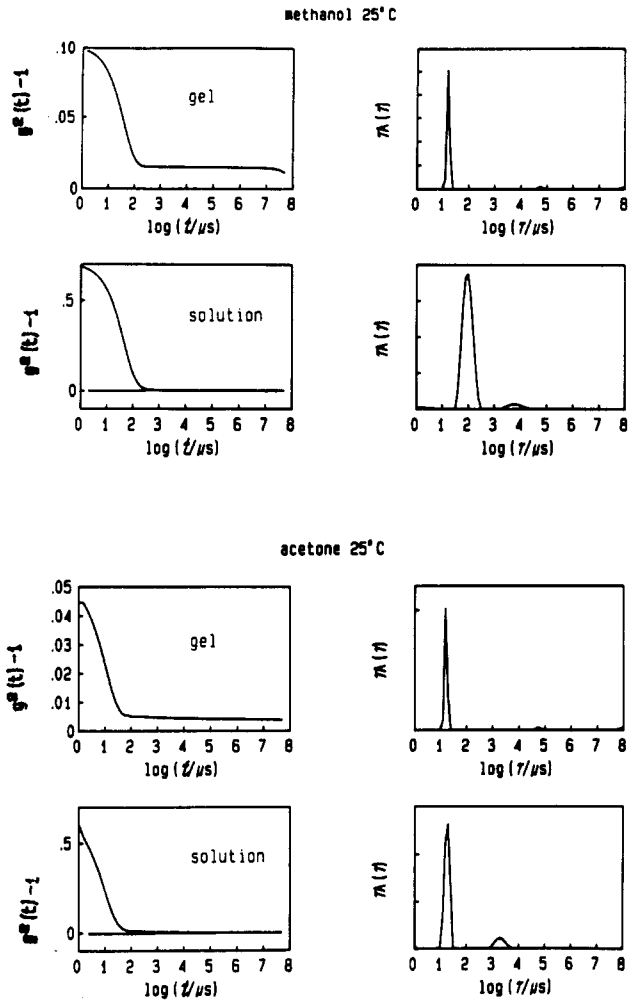

Figure 1. Autocorrelation functions $g^2(t)$ and corresponding relaxation time distributions $\tau A(\tau)$ versus $\log \tau/\mu s$, for solutions and gels in methanol and acetone at 25 °C. Angle = 90° and $C \approx 6\%$.

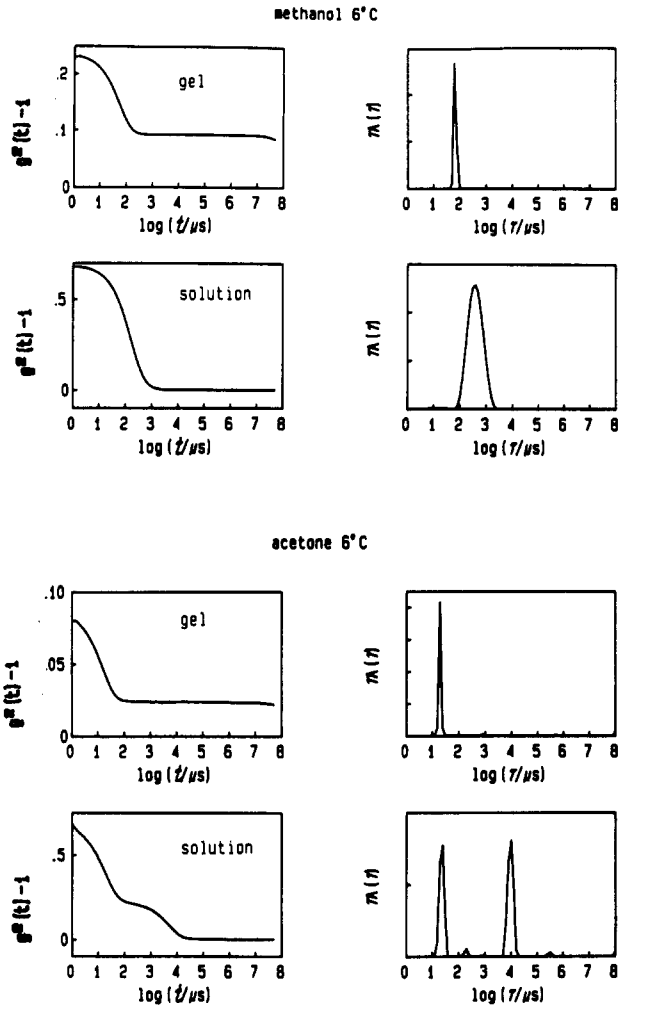

Figure 2. Corresponding data to those in Figure 1 but at 6 °C.

$4\pi^2 n_0^2 (dn/dC)^2 / N_A \lambda^4$, where n_0 is the solvent refractive index, and dn/dc, the refractive index increment (=0.132 mL/g in methanol at 25 °C and 0.104 in acetone at 25 °C).[17] The scattering function, 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.[18] There was no significant angular dependence of KC/R_θ in the range 45–135° for either gels or solutions. All measurements were made in concentration ranges in which multiple-scattering effects could be neglected. The weight-average molecular weight was M_W = 225 000, and the radius of gyration, R_g = 175 Å (acetone) and 159 Å (methanol), was estimated from the Flory–Fox equation using the intrinsic viscosity. The persistence length was estimated to be ≈23 Å.

Results and Discussion

Figure 1 shows autocorrelation functions for the PVAc solutions and gels in acetone and methanol at 25 °C together with the corresponding relaxation time distributions obtained by using inverse Laplace transformation. Figure 2 gives corresponding information for solutions and gels at 6 °C.

In both solutions and gels at 25 °C the decaying portions of the correlation functions are close to single exponentials whereas in the previously studied semidilute aqueous PVA solutions,[1] they were bimodal due to contributions from the translational motions of large (up to $R_H \approx 2000$ Å) ordered domains of PVA chains in the transient network in addition to diffusion of the individual chains. On the other hand, the correlation functions for the gels formed by cross-linking the PVA chains in semidilute aqueous solution with glutaraldehyde were strictly unimodal at all polymer concentrations and levels of cross-linking, establishing a high level of structural homogeneity.

Major differences between the correlation functions for the PVAc gels and those for the corresponding solutions are as follows:

1. The amplitude of $g^2(t)$ is always much lower for the gel than the solution.
2. With the gels in both acetone and methanol, there is always present a substantial base line deriving from scattering centers, which are apparently stationary on the time/distance scale of the experiments. See the correlation curves in Figures 1 and 2.
3. In the methanol solutions, the width of the gel mode peak is considerably broader than that for the corresponding gel.

Recent experiments on PVME gels in toluene[19] show, however, that "static" scatterers may be associated with a very long relaxation time ($\approx 10^3$ s) and thus reflect motions of large clusters in that system. Baselines were not observed in the correlation functions for the PVA gels swollen in water. Since the PVAc gels were prepared by acetylating the previously examined optically homogeneous PVA gels (singe-exponential relaxation), this finding suggests that the static scatterers are not dust particles trapped in the structure, but instead the scattering is associated with a few regions of local order. As pointed out by Patterson,[20] chains must disentangle to fully relax a concentration fluctuation, and some partially relaxed

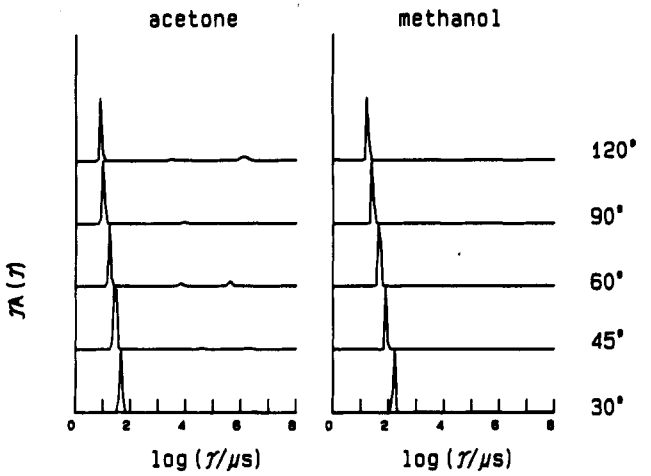

Figure 3. Decay time distributions for the PVAc gels of $C \approx 6\%$ in acetone and methanol at 25 °C at the angles shown. The relaxation rate is q^2-dependent in each case.

regions will be frozen into the network on formation of gel. This feature could, alternatively and more trivially, be due to inhomogeneities deriving from incomplete acetylation. As pointed out by Mallam et al.,[21] gels inevitably contain defects. It was noted that the base lines are more pronounced in both solvents in the low-temperature experiments. However, since there is no significant angular dependence of the total scattered intensity, one may conclude that their number density is very small.

We note here that the relaxation modes are diffusive in all cases: i.e., the relaxation frequency is linearly dependent on the square of the scattering vector, q. Figure 3 shows relaxation time distributions at different q-values for the gels in methanol and acetone at 25 °C.

Relaxation time distributions are shown in Figure 4 for semidilute solutions in both solvents at 6 and 25 °C and at different measurement angles. In the solutions, the investigated concentration range corresponds to 3.1–8.5C^* (acetone) and 2.3–6.2C^* (methanol). The distributions in methanol are almost unimodal at 25 °C and, perhaps unexpectedly, also at 6 °C under Θ-conditions where one might have anticipated the participation of slow processes similar to the structural relaxations found in semidilute solutions.[14] Whereas at 25 °C PVAc in solution in acetone is unimodal, at 6 °C the correlation function becomes bimodal due to the additional presence of a slow mode (q^2-dependent) possibly denoting diffusional motions of molecular domains or clusters. In this respect the system is markedly similar to the PVA solutions in water.[1] (As discussed previously,[22,23] in the case of a semidilute polymer solution containing two polymers differing in molecular weight, two modes of relaxation may be observed since the signal from one component modulates that of the other. The fast mode describes the cooperative relaxations of the transient network while the slow mode corresponds to interdiffusion of the two polymers.) Apparent radii of gyration corresponding to the slow mode were estimated at different concentrations from the ratio of the relative amplitudes according to ref 11 on the assumption that the fast mode corresponds to the network mode of the semidilute solution and has an amplitude that is angle-independent. The size of the clusters grows with increasing concentration as shown in Figure 5. It is possible that this trend in acetone is related to incipient crystallization of the polymer. Since acetone is a good solvent for PVAc, cluster formation might suggest some specific solvent interaction between acetone and the PVAc chains. Domain formation in PVAc has earlier been recognized, and

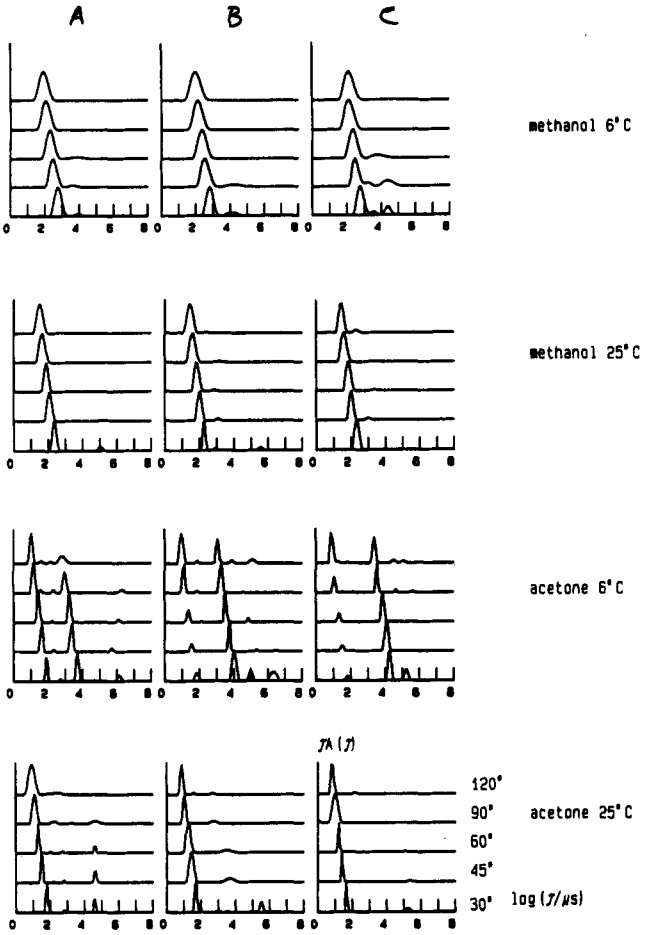

Figure 4. Relaxation time distributions for semidilute solutions at three concentrations in methanol (4.1, 5.9, and 8.0% respectively A, B, and C) and acetone (4.0, 6.1, and 7.9% respectively A, B, and C) at the temperatures shown and at the angles indicated.

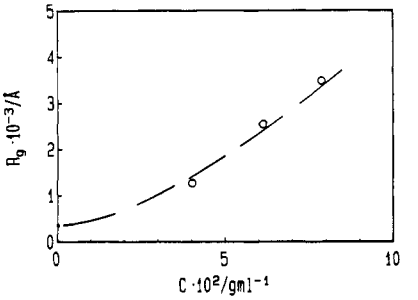

Figure 5. Apparent radii of gyration for the slow component in acetone solutions at 6 °C (derived from the ratio of relative amplitudes as described in ref 11 shown as a function of concentration.

this propensity has led to considerable interest in connection with the ability of PVAc systems to form liquid crystals.

Screening lengths: Scaling theory[24] assumes a unique screening length in entangled systems. However, experimental findings in semidilute solutions[25,26] have shown that the dynamic screening length (ξ_H) is approximately twice the excluded-volume length scale (ξ_a). Muthukumar and Edwards[27] moreover, stress the fundamental differences in the origins of these length scales. In the various theoretical approaches, including the recently developed renormalization group theory (see, for example, ref 28), the effects of topological constraints (i.e., entanglements) have not been taken into account and the chains have been regarded as freely interpenetrating. This is

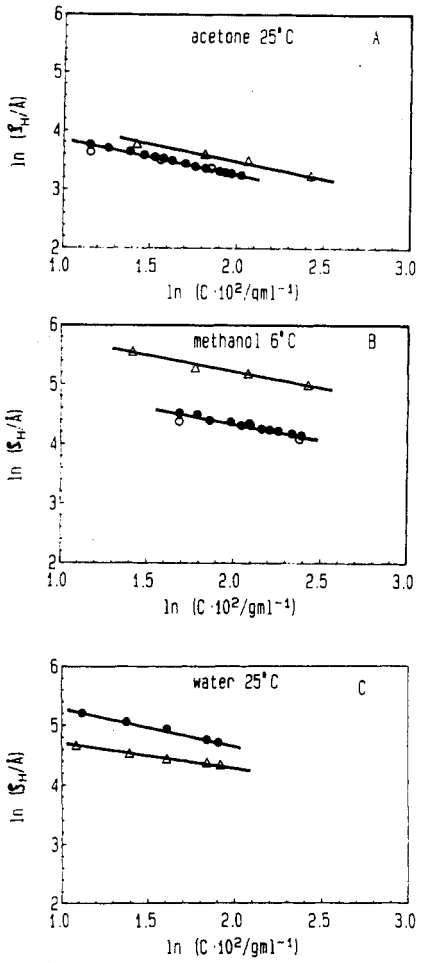

Figure 6. Concentration dependence of the dynamic polymer–polymer correlation length (ξ_H) for (A) PVAc solutions and gels in acetone at 25 °C (filled circles, gels prepared by controlled evaporation; open circles, gels synthesized at different concentrations; triangles, solutions of PVAc); (B) PVAc solutions and gels in methanol at 6 °C (Θ-state), with symbols as in A; (C) PVA solutions and gels in water (filled circles, gels; triangles, solutions; (concentration exponents given in Table I).

obviously unrealistic for gels. While entanglements will be of no consequence for the static properties, they should strongly affect ξ_H; however, no predictions have been made in this regard for permanent gels.

Experimental resolution of the relationship between the static and dynamic correlation lengths is not straightforward. While the cooperative diffusion coefficient, and hence ξ_H, can be determined with good precision by dynamic light scattering, the presence of static scatterers in the gels (see the base line for the gels; Figures 1 and 2) complicates the determination of ξ_s using intensity light scattering and hence prohibits a meaningful discussion of the ratio (ξ_H/ξ_s) at this juncture. SANS should provide the best alternative route to the static length scale. Thus, we restrict the present discussion to the dynamic length. Figure 6 compares dynamic correlation lengths in the different systems. In estimating the correlation length, correction has been made for solvent backflow due to the finite volume of polymer by dividing the relaxation frequencies by $1 - \Phi$, where Φ is the polymer volume fraction, and correction was also made for partial heterodyning, which is significant for the gels.[30] The dependence of the dynamic correlation length on concentration is shown in a log–log plot for both solvents (Figure 6A,B) and may be compared with data obtained from the PVA gel in water (Figure 6C).

Table I
Hydrodynamic (ξ_H) Screening Lengths and Concentration Exponents for the Dynamic Correlation Length ($\xi_H \sim C^{-\nu}$) for PVAc Gels and Solutions in Methanol and Acetone and for PVA in Water[a]

	solution	gel
Hydrodynamic Screening Lengths		
PVAc		
acetone (25 °C)	38	29
methanol (25 °C)	91	83
methanol (6 °C)	195	105
PVA		
water (25 °C)	81	122
Concentration Exponents		
PVAc		
acetone (25 °C)	0.5_3	0.6_1
methanol (6 °C)	0.5_3	0.5_4
methanol (25 °C)	0.5_0	0.6_5
PVA		
water (25 °C)	0.3_9	0.7_2

[a] The length scales are given for a polymer concentration of $C \approx 6 \times 10^{-2}$ g mL^{-1}.

Different concentrations of the gel in Figure 6A,B have been achieved in two ways:

1. One way is by cross-linking PVA chains in water solutions differing in (semidilute) concentration, with subsequent complete acetylation of the PVA gel thus formed; see the Experimental Section). Here, the number of entanglements "frozen" in the gel structure increases with concentration (unfilled circles in Figure 6A,B). Thereafter the gels were allowed to swell to equilibrium in the respective solvent (acetone, methanol).

2. The other way is by allowing slow evaporation to occur stepwise from the PVAc gel swollen at equilibrium in the organic solvent in question, followed by sealing the cell and allowing the gel to reequilibrate for 24 h prior to each measurement. The filled circles in Figure 6A,B thus refer to gels having a constant number of trapped entanglements at these concentrations.

The results show that over the concentration ranges used here and with gels of low cross-linking density (≈1%), distinction between 1 and 2 is irrelevant.

In both organic solvents, the dynamic length at any given concentration for the gels is significantly smaller than that for the solution of the same concentration (see also Table I), the effect being greatest in the Θ-system. In PVA in water (Figure 6C), on the other hand, the reverse trend was found,[1] an effect that is presumed to be related to H-bonding in the aqueous system. Since the gels in the organic solvents have been allowed to swell freely in excess solvent to equilibrium, the ultimate restriction to further swelling is imposed by the presence of the cross-links.

According to the C^* theorem of de Gennes,[24] gels swollen at constant pressure, as is the case here, should maintain a concentration proportional to C^*. The correlation length should then be proportional to the radius of gyration of the single coil having the same molecular weight as that between cross-links in the gel. The latter may be estimated to be $M \approx 8650$, corresponding to $R_g \approx 60$ Å in acetone at a cross-link density of 1%. From the data summarized in Table I it is seen that the correlation length for the gel (at an arbitrary concentration of 0.06 g mL^{-1}) is very short in the good solvent, acetone (29 Å), and considerably longer under Θ-conditions (105 Å) in methanol, 6 °C. This is in accord with the difference in solvent qualities and the reflected degrees of macroscopic swelling of the gels. The ratio of the radii of the cylindrical gels in the two solvents is 1.36 at 25 °C. The correlation length in the acetone-swollen gel does not greatly exceed the persistence length

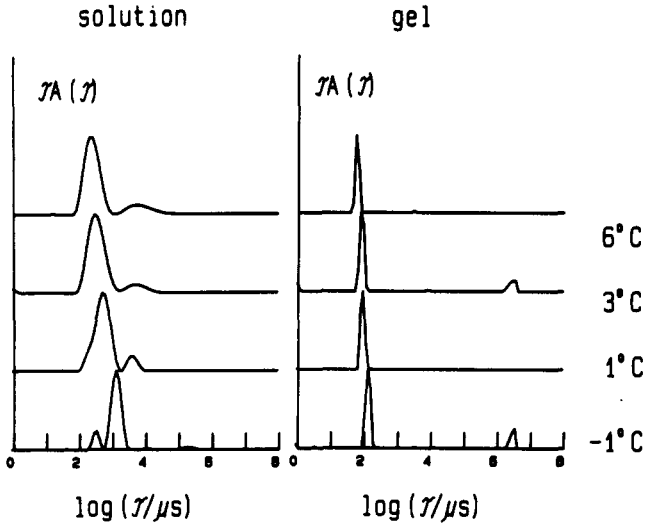

Figure 7. Relaxation time distributions in methanol at temperatures at and below the Θ-temperature of 6 °C for a solution (C = 8.0%) and a gel (C = 10.8%) at angle 60°. A shift of (T/η_0) has been made on the log τ axis at each temperature to facilitate comparison.

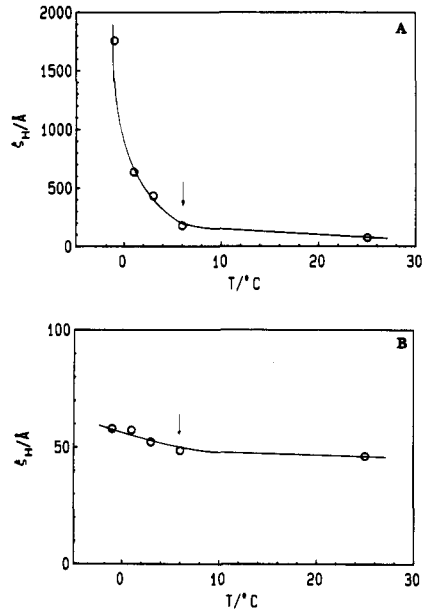

Figure 8. Temperature dependence of the dynamic correlation length for (A) PVAc solutions (C = 8.0%) and (B) gels (C = 10.8%) in methanol.

for the chains (estimated as ≈23 Å for PVA). The correlation length in the present gels is not equal to the distance between chemical cross-linking points because the gels were prepared by cross-linking semidilute solutions of PVA; the transient entanglements presnt at each concentration are "frozen" in the gel structure.

In the case of solutions, increasing concentration leads to greater interpenetration of molecular coils and consequently a decreasing correlation length. The same effect is present in gels, even though the presence of permanent cross-links must modify the way in which chains are able to entangle. In good solvents one expects a concentration exponent in the vicinity of −0.7 and −1 in a Θ-solvent. The concentration exponents in the solution and gel systems (Table I) are lower than anticipated and remarkably similar. Noteworthy are the low exponents in the Θ-system. The earlier report of Geissler et al.[29] on polyacrylamide gels in a water/methanol Θ-mixture indicated an exponent of close to unity, although this system was complicated by nonexponential correlation functions.

Measurements were also made as a function of temperature below the Θ-temperature of 6 °C in methanol on the gel (C = 10.8%) and solution (C = 8.01%). The measurements have been made on the gel at essentially constant concentration, i.e., after only a 30-min equilibration subsequent to temperature change. Figure 7 shows relaxation time distributions under the various conditions. A shift of T/η_0 has been made at each temperature on the log τ axis relative to the data at 6 °C, in order to facilitate comparison. In the case of the solutions, the main peak describing the transient gel is substantially broader than that for the corresponding gel and is displaced toward longer relaxation time. While the solutions show a tendency to clouding at −1 °C, the gels remain optically clear at this temperature.

Parts A and B of Figure 8 show the temperature dependence of the dynamic correlation length for solutions and gels. In the solution ξ_H increases dramatically, as would be expected[13c] when the temperature falls below 6 °C. In the gel of the same concentration there is a very small increase in ξ_H over the same temperature range. Thus cross-linking inhibits polymer–polymer interactions and serves to stabilize the structure.

References and Notes

(1) Fang, L.; Brown, W. *Macromolecules* **1990**, *23*, 3284.
(2) Zrinyi, M.; Molnar, T.; Horvath, E. *Polymer* **1981**, *22*, 429.
(3) Geissler, E.; Horkay, F.; Hecht, A. M.; Zrinyi, M. *J. Chem. Phys.* **1989**, *90*, 1924.
(4) Horkay, F.; Hecht, A. M.; Geissler, E. *J. Chem. Phys.* **1989**, *91*, 2706.
(5) Horkay, F.; Zrinyi, M. *J. Macromol. Sci., Phys.* **1986**, *B25* (3), 307.
(6) Horkay, F.; Geissler, E.; Hecht, A.-M.; Zrinyi, M. *Macromolecules*, in press.
(7) Polik, W. F.; Burchard, W. *Macromolecules* **1983**, *16*, 978.
(8) Brown, W. *Macromolecules* **1984**, *17*, 66.
(9) Brown, W. *Polymer* **1985**, *26*, 1647.
(10) Eisele, M.; Burchard, W. *Macromolecules* **1984**, *17*, 1636.
(11) Sedlák, M.; Koňák, C.; Štěpánek, P.; Jakeš, J. *Polymer* **1987**, *28*, 873.
(12) Geissler, E.; Hecht, A. M.; Duplessix, R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 225.
(13) (a) Munch, J. P.; Candau, S. J.; Herz. J.; Hild, G. *J. Phys.* (*Les Ulis, Fr.*) **1977**, *38*, 971. (b) Candau, S. J.; Bastide, J.; Delsanti, M. *Adv. Polym. Sci.* **1982**, *44*, 27. (c) Candau, S.; Munmch, J. P.; Hild, G. *J. Phys.* (*Les Ulis, Fr.*) **1980**, *41*, 1031.
(14) Nicolai, T.; Brown, W.; Johnsen, R. M.; Štěpánek, P. *Macromolecules* **1990**, *23*, 1165.
(15) Jakeš, J., to be published.
(16) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.
(17) Elias, H. G.; Vogt, P. *Makromol. Chem.* **1972**, *157*, 263.
(18) Pike, E. R.; Pomeroy, W. R. M.; Vaughan, J. M. *J. Chem. Phys.* **1975**, *62*, 3188.
(19) Lodge, T.; Štěpánek, P., unpublished data.
(20) Patterson, G. D. *Rubber Chem. Technol.* **1989**, *62*, 503.
(21) Mallam, S.; Horkay, F.; Hecht, A.-M.; Geissler, E. *Macromolecules* **1989**,*22*, 3356.
(22) Benmouna, M.; Benoit, H.; Duval, M. *Macromolecules* **1987**, *20*, 1107, 1112.
(23) Brown, W.; Zhou, P. *Macromolecules* **1989**, *22*, 4031.
(24) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(25) Brown, W.; Mortensen, K. *Macromolecules* **1988**, *21*, 420.
(26) Brown, W.; Nicolai, T. *Colloid Polym. Sci.*, **1990**, *268*, 977.
(27) Muthukumar, M.; Edwards, S. F. *Polymer* **1982**, *23*, 345.
(28) Ohta, T.; Oona, T.; Freed, K. *Phys. Rev.* **1982**, *A25*, 2801.
(29) Geissler, E.; Bohidar, H. B.; Hecht, A.-M. *Macromolecules* **1985**, *18*, 949.

(30) $D_{corr} = D/(1 - B/2)$, where B = baseline value.