Microrheology of Poly(vinyl alcohol) Aqueous Solutions and Chemically Cross-Linked Gels

Tetsuharu Narita, Alexandra Knaebel, Jean-Pierre Munch, and Sauveur Jean Candau*

Laboratoire de Dynamique des Fluides Complexes, 4, rue Blaise Pascal,
67070 Strasbourg Cedex, France

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ABSTRACT: The motion of probe particles in aqueous solutions of linear and branched poly(vinyl alcohol) (PVA) and in chemically cross-linked PVA gels has been studied by diffusing-wave spectroscopy. At long time scales the measurements allow to determine the effect of the cross-linking ratio on the macroscopic viscosity of sols and the shear modulus of gels. The local shear modulus of gels as obtained from the characteristic length of the Brownian cage was found to agree with that measured by classical rheometry and dynamic light scattering. The behavior of the mean-square displacement of the probe particles at short time indicates that the high-frequency viscoelasticity is the same for solutions and highly cross-linked gels whereas gels with low cross-linking ratio exhibit a lower storage modulus.

Introduction

The advent of diffusing-wave spectroscopy (DWS)[1−5] and particle-tracking microrheology[6,7] has allowed to probe the high-frequency viscoelastic behavior of polymer gels, entangled solutions, and concentrated colloidal suspensions. The main advantage of these techniques resides in the fact that they allow an "in situ" determination of the viscoelastic moduli over an extended dynamic range.

In a DWS experiment, multiple light scattering is used to measure the motion, driven by thermal fluctuations, of probe particles embedded in the investigated medium. In polymeric gels, the concentration fluctuations are geometrically and topologically constrained by the presence of cross-links. Such systems are nonergodic, and the study of their dynamic properties by light scattering is rendered difficult by the fact that they explore only a fraction of all their possible configurations. Therefore, ensemble averages over all the configurations have to be performed when measuring the dynamic structure factor. The formalism that was developed first for interpreting single dynamic light scattering (DLS) in nonergodic media was recently extended to the DWS experiments.[5]

From the mean-square displacement $\langle \Delta r^2(t) \rangle$ that is extracted from the measured autocorrelation function $g^{(2)}(t)$ of the light multiple scattered by the probe particles, one can obtain viscoelastic moduli and creep compliance at time scales as short as 10^{-5} s. From these measurements one can gain insight into the local macromolecular motion at short length scales and short time scales.

Several experimental studies of the viscoelasticity of gels using DWS and/or particle-tracking microrheology have been reported. Most of the studies have concerned networks of actin filaments which are long semiflexible polymers.[2,3] The main issues addressed in these studies concerned the scaling with concentration of the small frequency plateau modulus and the scaling with frequency of the high-frequency complex modulus resulting from the small-amplitude, large frequency lateral fluctuations of actin filaments between entanglements and/or cross-links.

Chemically cross-linked polyacrylamide[7] and poly(acrylic acid) gels[5] have also been investigated by means of microrheological techniques. The results obtained showed the suitability of theses techniques to investigate both dissipative short-time properties and elastic moduli of permanently cross-linked gels.

In this paper, we study the effect of cross-linking on the short-time motion of poly(vinyl alcohol) chains in solutions and gels. In particular, we investigate the evolution of the time dependence of the mean-square displacement of the probe particles when passing progressively from solutions of linear chains to highly cross-linked gels. We also compare measurements of the shear modulus of gels by means of DWS, dynamic light scattering (DLS), and classical mechanical measurements.

Experimental Section

Materials and Preparation of Gels. Poly(vinyl alcohol) (PVA; molecular weight: 95 000; degree of deacetylation: 95 mol %) was purchased from Acros Organics. Glutaraldehyde (GA, 8% aqueous solution) was obtained from Sigma and hydrochloric acid from Merck Eurolab division PROLABO (France). Polystyrene microspheres (diameter: 107 and 535 nm) were obtained from PolySciences, Inc.. All the chemicals were used as received. Stock solutions of PVA (10 or 13 wt %) were prepared by dissolving PVA powder in water at 90 °C. PVA gels were prepared by addition of GA (the cross-linking ratio R_c, defined as the molar ratio of GA to repeating units of PVA, is between 0.001 and 0.01) as cross-linker, at acidic condition (pH $\approx$ 2, adjusted by HCl). The final PVA concentration was adjusted to 2−10% (w/w). All the experiments were performed in a controlled environment at 25 ± 0.5 °C.

DLS Measurements in PVA Solutions and Gels. The coherent source was a Spectra Physics 2000 laser, operated at $\lambda = 488$ nm. The correlation function of the scattered light at various scattering angles θ ($30° \le \theta \le 120°$) was calculated by an ALV5000 correlator. The coherence factor of the experimental setup was measured with a reference latex suspension and was equal to 0.97 ± 0.02.

Single light scattering experiments were performed on both PVA solutions and gels with and without probe particles. The

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* Corresponding author. e-mail: candau@fresnel.u-strasbg.fr.

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latter were latex particles with diameter 107 nm dispersed in the solution prior to gelation at a concentration of 10^{-2}%. Gels were prepared directly in cylindrical light scattering cells (12 mm in diameter, 130 mm in length). To obtain the ensemble average of the scattered signal over many scattering volumes in the gel, the sample cell was rotated continuously. The experiment provides the ensemble averaged autocorrelation function $g^{(2)}(t)$ of the scattered light intensity. From $g^{(2)}(t)$ one obtains the dynamic structure factor $g^{(1)}(t)$ through $g^{(1)}(t) = [g^{(2)}(t) - 1]^{0.5}$.

DWS Measurements in PVA Solutions and Gels. DWS measurements were carried out on PVA samples containing latex particles as probes. The laser beam at $\lambda = 488$ nm from an argon ion laser (Spectra Physics 2020) was expanded to about 1 cm diameter at the sample. The diffused light was collected by a single-mode optic fiber placed in the axis of the beam for transmitting geometry or placed in backscattering cone for backscattering geometry. The intensity autocorrelation function of the diffused light was calculated using a BI9000 correlator. To obtain the ensemble average of the scattered intensity, the optical fiber detecting the light was oscillated at 10 mHz, so that the scattering signal from different positions was recorded. According to the DWS theory by Weitz and Pine,[1] one can extract the mean-square displacement $\langle \Delta r^2(t) \rangle$ from the measured autocorrelation $g^{(2)}(t)$ of the light multiple scattered. A detailed theoretical presentation of DWS in nonergodic systems was reported previously.[5] PVA solutions and gels containing latex particles (535 nm in diameter, 1%) were prepared in light scattering cells (21 mm in diameter, 2 mm in thickness).

Macrorheological Measurements (Mechanical Rheometry). For the comparison with optical microrheological measurements, mechanical macroscopic measurements were performed in PVA solutions and gels. A stress-controlled mechanical rheometer (Haake RS600) was used with a cone−plate geometry (22 or 60 mm in diameter, $a = 0.5°$) to measure the steady shear viscosity of PVA solutions and the dynamic shear modulus of gels. To avoid systematic errors on the data obtained for gels, gelation was carried out between the cone and the plate. The completion of the cross-linking reaction was checked by monitoring the storage modulus G' and the loss modulus G'' with time. Both moduli reached plateau values within 6 h at the conditions of the experiments. After each run, as the sample was removed, it was checked that the PVA gel adhered to the surfaces of the cone and plate, with no presence of lubrication water layer at the interface. Frequency sweeps of $G'(\omega)$ and $G''(\omega)$ were made at constant stress (0.3−3 Pa in the linear regime) at low strain (<3%).

Results and Discussion

DLS from Solutions and Gels of PVA. We first present the main thermodynamic and dynamic characteristics of the systems studied.

We have investigated by rheology and DLS solutions of linear PVA macromolecules in the range of concentrations extending from 2% to 10%. Figure 1 shows the variation of the relative viscosity η_p/η_0 where η_p is the viscosity of the solution and η_0 the viscosity of the water as a function of the polymer concentration C_p. The crossover concentration C^* between dilute and semidilute regime can be estimated from the intrinsic viscosity according to $C^* = [\eta]^{-1}$.[8] For this system we find $C^* \cong 1.3\%$. The concentrations of the solutions used as precursors for the gel formation were larger than C^*, and therefore the PVA chains were overlapping each other. It is seen in Figure 1 that the relative viscosity increases smoothly up to a concentration $C_e \cong 4.3\%$, beyond which it increases more steeply. In the high concentration range the relative viscosity follows a power law of C_p with an exponent 4.5. Such behavior has been previously reported for other polymer solutions in good solvent.[9,10] The concentration C_e is the concentration beyond which entanglements form and the reptation model applies. C_e is generally 3−10 times larger than C^*.[11] The experimental value of the exponent of the power law of $\eta(C_p)$ is significantly larger than the value 3.92 predicted by the theory,[8] and no explanation has been proposed up to now for such discrepancy. Below C_e the dynamics of the system is Rouse−Zimm like, and the concentration dependence is much weaker. A consequence of the above results that might be relevant for the understanding of the properties of the gels is that gels prepared at concentrations ≥5% are made from preentangled solutions. This is quite favorable to the presence within the gel of trapped entanglements.

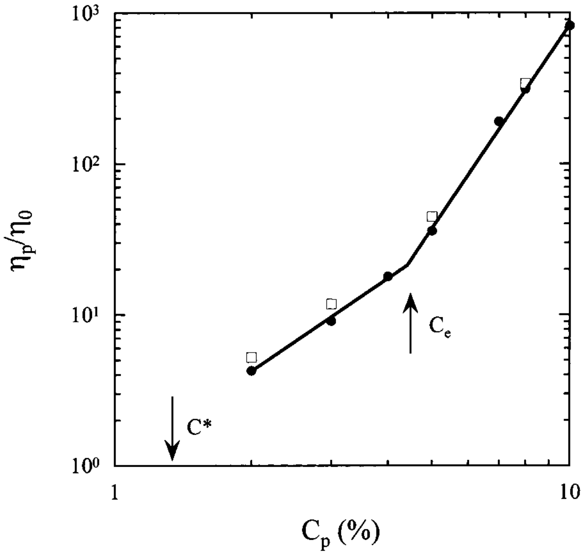

Figure 1. Concentration dependence of the relative viscosity of PVA solutions: filled circles, classical macroscopic rheometry (without latex); open squares, DWS (with 1% latex). The solid line drawn through the data above C_e has a slope of 4.5.

Figure 2a shows typical examples of normalized single dynamic light scattering intensity autocorrelations of a PVA aqueous solution at various scattering angles. As several authors have previously reported,[12,13] the intensity correlation function is bimodal. We observed that the q dependences of the characteristic time of the fast mode τ_f and that of the slow mode τ_s were $\tau_f \sim q^2$ and $\tau_s \sim q^x$, where x is between 2 and 3, respectively. The fast mode results from the collective fluctuations characterized by a diffusion coefficient $D_c = (\tau_f q^2)^{-1}$. The slow mode has been observed in a number of systems including aqueous polyelectrolytes solutions and polymer solutions in marginal solvent.[14] This slow mode is believed to be due to the formation of aggregates. In the case of PVA solutions it was suggested that paracrystalline domains were formed by hydrogen bonding.[15] The large value of the exponent x suggests that the slow mode is due to the presence in the system of large clusters. The average size of these domains, as estimated from τ_s, is of the order of 1 μm. It is difficult to remove the aggregates by repeated filtration, presumably because the polymers form temporary clusters via hydrogen bonding and/or hydrophobic interaction. It was also found that the amplitude of the slow mode depends somewhat on the thermal history of the sample. This was also inferred from viscosity measurements that revealed aging phenomena in PVA solutions.[15,16] Since concentrated urea is reported to break the hydrogen bonding of PVA,[17] we measured the q dependences of

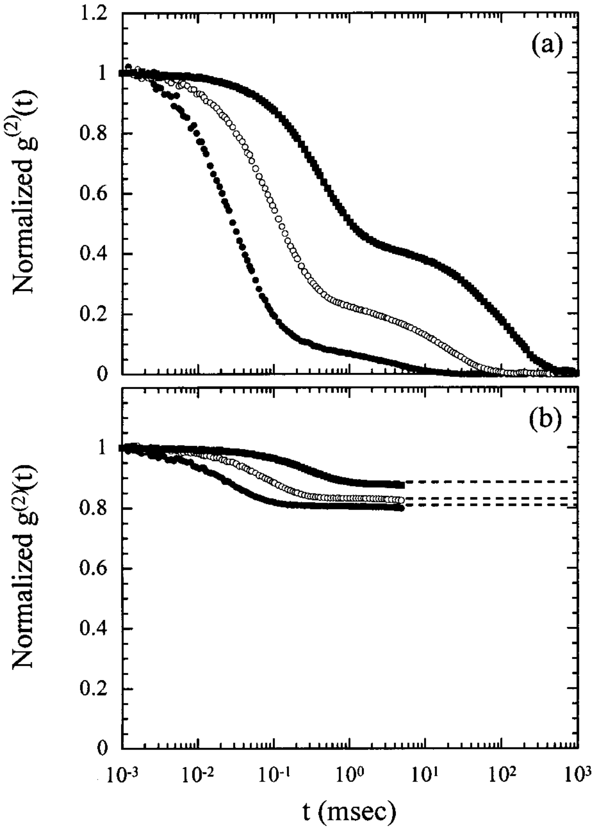

Figure 2. Normalized dynamic structure factors for (a) a PVA solution (5%) and (b) a PVA gel (5%, $R_c = 0.01$) at various scattering angles. Scattering angle: 120° (filled circles), 60° (open circles), and 30° (filled squares).

the fast and the slow modes in the presence of urea (30% and 50%). It was found that the relaxation time of the fast mode is almost independent of urea concentration, but the slow mode was not suppressed, its characteristic time increasing with the urea concentration. However, the presence of such aggregates whose concentration is very small should not affect the properties of solutions and gels.

The variation of D_c with PVA concentration is plotted in Figure 3. One observes a monotonic increase of D_c with concentration which indicates that the solutions are semidilute. The asymptotic regime where D_c should scale like $C^{0.67}$ is not reached, but it is known that the dynamical scaling exponents can be reached only with polymers with very large molecular weight.[18]

Turning now to the cross-linked systems, Figure 4 shows the domain of existence of PVA gels in the diagram PVA concentration−cross-linking ratio R_c. The lower the PVA concentration, the higher the amount of cross-linker required for gelation. High cross-linking ratio induces a shrinkage of the gel during the cross-linking reaction with expulsion of water.

Figure 5 shows equilibrium concentrations C_{eq} of PVA gels prepared at 5% and 8% as a function of the cross-linking ratio R_c. Increasing R_c as well as the initial PVA concentration results in an increased C_{eq}. An approximate expression of the Flory's prediction for the swelling equilibrium concentration for good solvent condition is[19]

$$C_{eq} \propto C_0^{2/3} N_c^{-3/5} \propto C_0^{2/3} R_c^{3/5} \qquad (1)$$

where C_0 is the concentration of the polymer in its

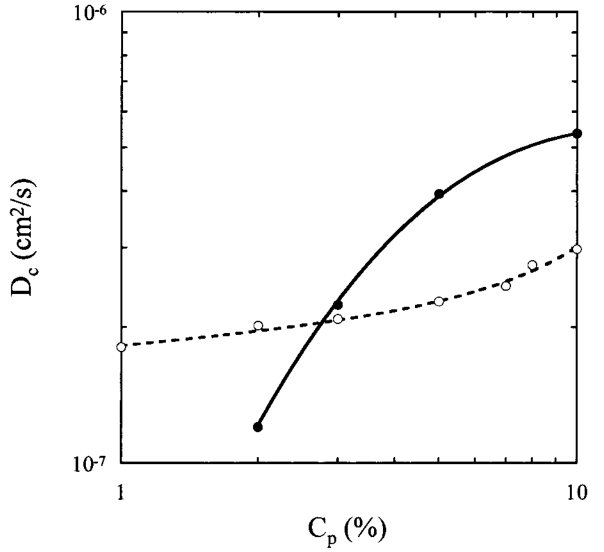

Figure 3. Cooperative diffusion coefficient D_c of PVA solutions (open circles) and gels (filled circles, cross-linking ratio R_c = 0.01) as a function of PVA concentration. Scattering angle: 30°.

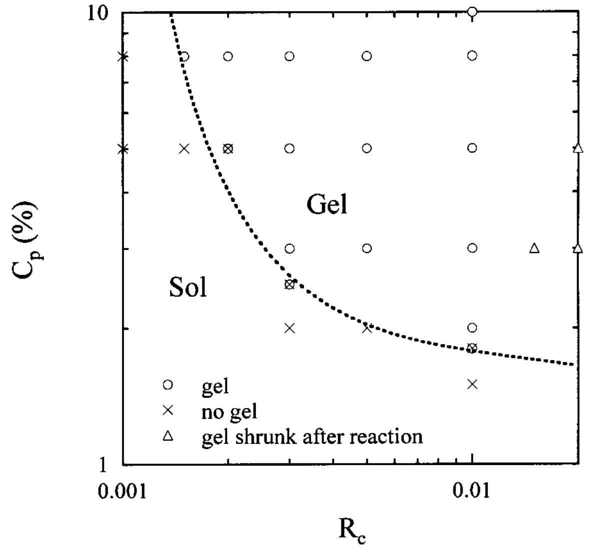

Figure 4. Diagram of gelation of PVA cross-linked by GA.

reference state which is taken generally to be the concentration of preparation, and N_c is the number of monomeric units between two consecutive cross-links, equivalent to $1/R_c$. Our results agree well with this prediction as shown in the inset, but this agreement might be fortuitous as the gels are likely to contain variable numbers of dangling chains and trapped entanglements depending on the cross-linker concentration.

Figure 2b shows normalized intensity autocorrelations of a PVA gel at various scattering angles. Contrary to what observed in PVA solutions, these functions do not go to zero at infinite time but reach a nonzero asymptotic value that increases such as exp($-q^2$). The latter represents the static component associated with the frozen-in density fluctuations in the gel. From the decay rate of the fluctuating component one can extract the cooperative diffusion constant D_c. The variation of D_c with polymer concentration for gels with cross-linking ratio 0.01 is represented in Figure 3. It can be seen that the curves representative of the variations of D_c in semidilute solutions and gels cross

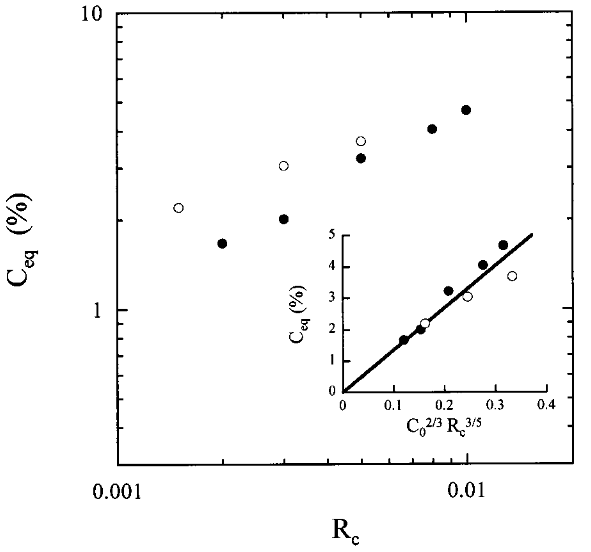

Figure 5. Equilibrium swelling concentration C_{eq} of PVA gels as a function of the cross-linking ratio. PVA concentration of preparation C_0: 5% (filled circles) and 8% (open circles). Inset: C_{eq} as a function of $C_0^{2/3}R_c^{3/5}$.

each other. In both entangled solutions and cross-linked gels D_c is given by the ratio $(K + {}^4/_3\mu)/f$, where K and μ are the bulk and shear moduli, respectively, and f is the effective frictional coefficient per monomer. The latter can be considered as identical in gels and semidilute solutions. As for the concentration dependence of the elastic modulus, it is likely to different in the two media. In fact, a behavior similar to that shown in Figure 2 has been already reported for polystyrene−benzene systems.[20] In particular, D_c was found always larger for gels at the equilibrium than for solutions. In this respect, it must be noted that the PVA gels prepared at high concentration approach their equilibrium condition.

DWS from PVA Solutions and Gels Containing Latex Particles. Measurements by DWS of the latex particle motion contained in gels and solutions allow to investigate the viscoelastic properties of such systems in a wide range of time. In particular, the short-time behavior is conveniently attained by DWS. Figure 6 shows the dynamic structure factors obtained for dispersions of latex particles (535 nm in diameter) in water, PVA solutions, and gels and measured in both backscattering and transmission geometries. For water and polymer solutions the structure factor goes to zero at long time. For the polymer solution, the representative curves are shifted toward the right with respect to that of water, indicating a slower diffusion of the particles through the medium. For the gels, the dynamic structure factor does not go to zero at infinite time. The plateau value increases upon increasing the cross-linking ratio, indicating that the particle motion is more restricted due to an increased modulus of the gel.

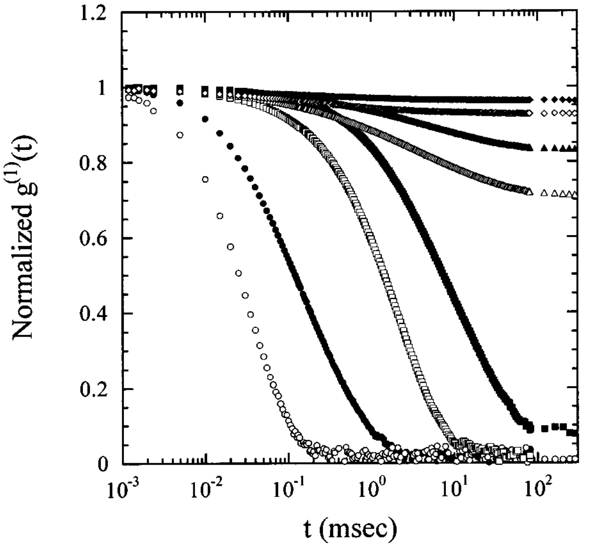

Figure 6. Normalized dynamic structure factors for PVA solutions and gels containing latex particles measured by DWS. Latex diameter: 535 nm. Latex concentration: 1%. Open symbols: backscattering geometry; closed symbols: transmitting geometry. Circles, water; squares, polymer solution (C_p = 5%); triangles, gel (C_p = 5%; R_c = 0.002); diamonds, gel (C_p = 5%; R_c = 0.003).

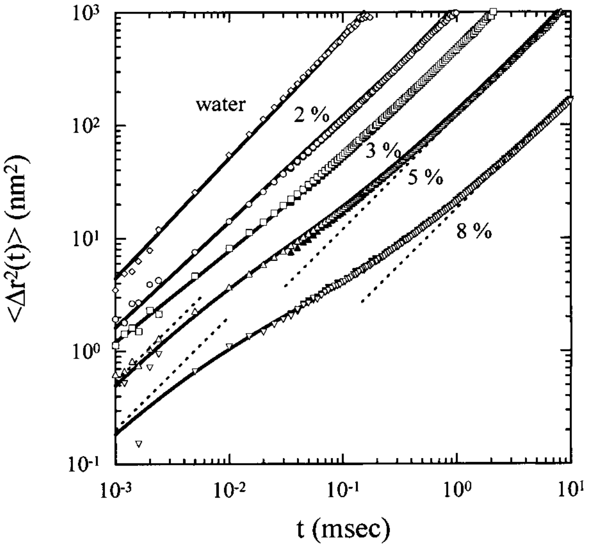

Figure 7. Mean-square displacement of latex particles in PVA solution of various concentrations as a function of time. Latex diameter: 535 nm. Latex concentration: 1%.

The dynamic structure factor was numerically inverted into the mean-square displacement of the probe particles, $\langle\Delta r^2(t)\rangle$. The results for solutions of linear PVA at various concentrations are plotted in Figure 7. The evolution of the particle motion as a function of the polymer concentration is clearly seen in that figure. At long time $\langle\Delta r^2(t)\rangle$ is proportional to the time at any PVA concentration studied but it decreases strongly with concentration. When the latex motion undergoes Brownian diffusion, $\langle\Delta r^2(t)\rangle$ is proportional to the time, $\langle\Delta r^2(t)\rangle = 6Dt$, where D is the diffusion coefficient of the latex in the solution. One can estimate the macroscopic viscosity of the system by using the Stokes−Einstein equation. The results thus obtained agree with those measured by macroscopic rheometry as shown in Figure 2. One can note that the viscosity of the solution is not modified by the addition of 1% of latex, which shows that the possible adsorption effects are weak.

At shorter times, the shape of the curves of representing the time dependence of the mean-square displacement depends strongly on the polymer concentration. In fact, it has been shown that the mean-square displacement is proportional to the shear creep compliance.[21] Therefore, the shape of the $\langle\Delta r^2(t)\rangle$ curves reflects the viscoelasticity of the sample. For a 2% solution, the particle motion is almost diffusive like in water with a linear dependence of $\langle\Delta r^2(t)\rangle$. In 3% PVA solutions, $\langle\Delta r^2$-

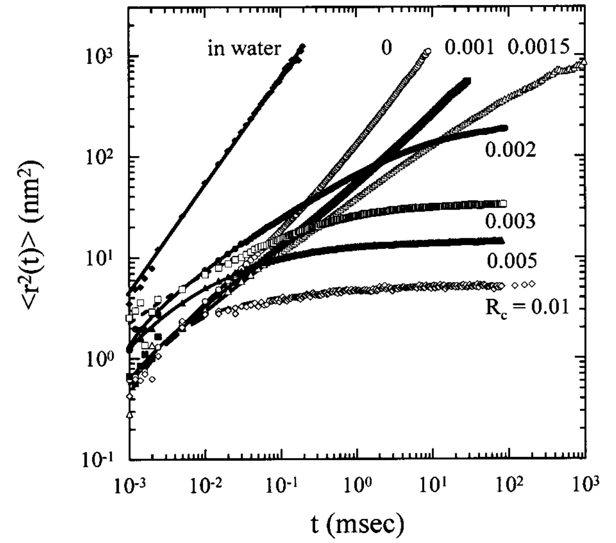

Figure 8. Mean-square displacement of latex particles in PVA solutions and gels with various cross-linking ratios as a function of time measured by DWS (transmission geometry). Numbers in the figure denote the cross-linking ratio R_c. The systems with $R_c \leq 0.0015$ are sols, and those with $R_c \geq 0.0020$ are gels.

$(t)\rangle$ deviates from the linear dependence. At short times ($t \leq 10$ ms) its variation can be fitted with a power law of time with an exponent of ~0.7. From the viscosity measurements, it was inferred that at this concentration the flexible polymer chains were unentangled and that the dynamics of the system should be described by a Rouse–Zimm model. In fact, the value of the experimental exponent 0.7 is larger than the Rouse value 0.5, which has been previously found for polyacrylamide gels. It is however close to the theoretical prediction of the nondraining Zimm model which is $^2/_3$. For semiflexible actin solutions, this exponent was found to be 0.75.[22]

For PVA solutions with $C_p \geq 5\%$ one observes an inflection point in the $\langle \Delta r^2(t)\rangle$ curves. One knows from the viscosity data of Figure 1 that in this regime the polymer chains are entangled. Therefore, the observed inflection reflects a plateau elasticity of the entanglements network corresponding to the confinement region in $\langle \Delta r^2(t)\rangle$. The smoothness of the plateau can be explained by the polydispersity of the chains and the fact that the concentration of the solutions studied is not far larger than the entanglement crossover C_e. At the shortest time, attained using DWS, the slope begins to rise toward unity without however reaching it. This reflects the approach to an effective molecular viscosity of the water and the polymer significantly larger than that of the water.

Next, we have investigated the effects of cross-linking on the displacement of the probe particles as a function of time. Figure 8 shows $\langle \Delta r^2(t)\rangle$ as a function of time for the latex particles in PVA systems with various amounts of cross-linker. Gelation is observed for cross-linking ratio ≥ 0.002 (Figure 1). At long time scales, the behaviors of $\langle \Delta r^2(t)\rangle$ of gels and solutions are totally different. For sols, $\langle \Delta r^2(t)\rangle$ increases continuously with time. Increasing the cross-linking ratio shifts the representative curves toward the longer time scales, indicating a slowing down of the motion of probe particles. In fact, the particle motion is diffusive only for solutions of linear polymers or of slightly branched polymers (cross-linking ratio of 0.001 and 0.0015). In that case, the long time behavior provides a measurement of the diffusion constant of the particles and subsequently of the macroscopic viscosity which is found to increase with the degree of branching. For higher cross-linking ratios $\langle \Delta r^2(t)\rangle$ is subdiffusive even at very long time, which suggests that these solutions are viscoelastic with a very large distribution of relaxation times extending up to the longest time scale probed.

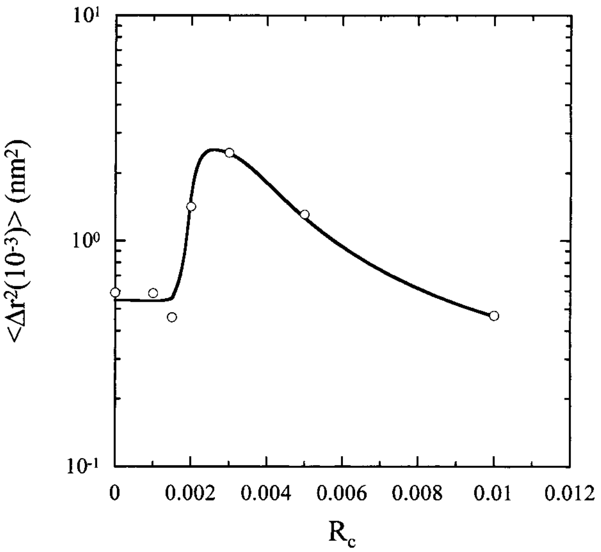

Figure 9. Mean-square displacement of latex particles in PVA solution at $t = 10^{-3}$ ms as a function of the cross-linking ratio R_c.

For gels, at long time scales, $\langle \Delta r^2(t)\rangle$ levels off at a certain value that decreases upon increasing cross-linking ratio. The mean-square displacement of the particles in gels is limited due to caging, and the maximum displacement is determined by the competition between the thermal energy of the particles and the elasticity of the network that is considered as a continuous medium since the particle size is much larger than the mesh size. $\langle \Delta r^2(t)\rangle$ can be expressed by this equation,

$$\langle \Delta r^2(t)\rangle = 6\delta^2[1 - \exp[-(t/\tau_c)^\gamma]] \tag{2}$$

where δ and τ_c are respectively the characteristic size and time of the Brownian cage, which are the characteristic spatial length and time required for the particles to explore the cage. The measurement of δ allows to estimate the shear modulus of the gel as discussed in the next section. The behavior of $\langle \Delta r^2(t)\rangle$ at short time is rather complex. The particle motion is subdiffusive for all systems as indicated by the exponent of $\langle \Delta r^2(t)\rangle$, which is less than 1. This is likely to be due to the contribution of the local subchains fluctuations to the complex modulus. A surprising observation that has already been reported[5] is that the mean-square displacement of the latex particles varies on a nonmonotonic way with the cross-linking ratio. In fact, the value of $\langle \Delta r^2(t)\rangle$ taken at the shortest time probed $t = 10^{-3}$ ms is maximum for a cross-linking ratio of 0.003 (Figure 9). One also observes that $\langle \Delta r^2(t)\rangle$ is about the same for highly cross-linked gels ($R_c = 0.001$) and the solutions of linear or slightly branched polymers. In this respect, it can be noted that the highly cross-linked gel at the concentration of 5% is close to its swelling equilibrium concentration. Many studies have shown that under these conditions the dynamic properties of both the solutions and the gels can be described in terms of a

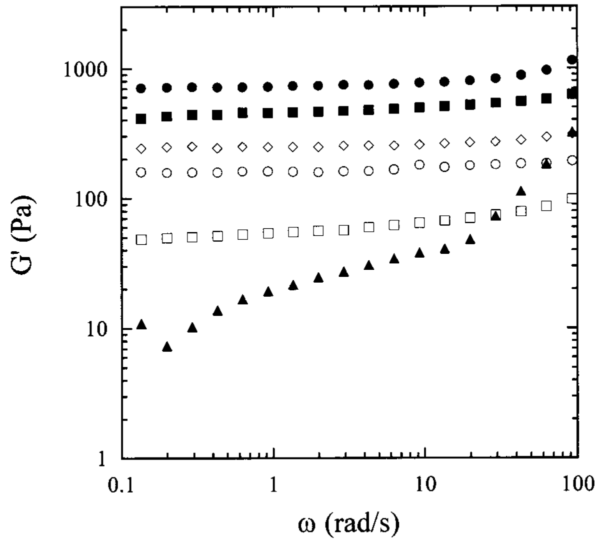

Figure 10. Frequency dependence of the storage shear modulus G' of PVA gels prepared at various conditions: open diamonds, $C_p = 5\%$, $R_c = 0.008$; open circles, $C_p = 5\%$, $R_c = 0.005$; open squares, $C_p = 5\%$, $R_c = 0.003$; filled circles, $C_p = 8\%$, $R_c = 0.005$; filled squares, $C_p = 8\%$, $R_c = 0.003$; filled triangles, $C_p = 8\%$, $R_c = 0.0015$.

single microscopic length ξ, which is the average distance between entanglements for solutions and average distance between cross-links (or trapped entanglements) for gels. For a gel at the swelling equilibrium, this correlation length is of the same order of magnitude as in a solution of linear polymer at the same concentration. The high frequency complex modulus and consequently $\langle \Delta r^2(t) \rangle$ at short time are controlled by the fluctuations within ξ, which explains the above result that $\langle \Delta r^2(t) \rangle$ is the same for solutions and gels.

For moderately cross-linked gels the swelling equilibrium concentration is much less than the actual concentration. There are two characteristic lengths: the average contour length between two cross-links which controls the zero frequency shear modulus and a smaller monomer−monomer correlation length, which can be approximated to be the length between two consecutive entanglements. If one wants to compare the gel to a solution, one should consider a solution of entangled branched polymers, for which we can assume that the density of effective entanglements is less than in a solution of linear polymers because of the presence of many dangling chains. This might allow for a larger displacement of the probe particles.

Elasticity of the Gels. In this section, we discuss the comparison of the values of the local storage shear modulus obtained by DWS with those measured by macroscopic rheometry and by single light scattering. Figure 10 shows the frequency dependence of the shear modulus G' of PVA gels measured by classical macroscopic rheometry. It is observed that an increase of the PVA concentration and/or the cross-linking ratio increases G'. It is also seen that G' does not strongly depend on frequency except for the gel with very low cross-linking ratio ($R_c = 0.0015$). One can consider that this gel contains many dangling chains that contribute to G' in the whole frequency range.

DWS experiments allowed us to estimate the local shear modulus μ of the PVA gels from the value of the maximum mean square displacement δ^2, arguing that the work necessary for a particle of radius R to move over δ is equal to the thermal energy k_BT of the particle, so that

$$\mu \cong \frac{k_B T}{6\pi R \delta^2} \tag{3}$$

In fact, as discussed by Schnurr et al.,[7] the above expression is strictly valid only at time scales which are short enough so that the solvent and the network move as one at scales large when compared with the mesh size of the network. The gel behaves as an incompressible fluid below a crossover time

$$\tau_i \cong \frac{\eta R^2}{G \xi^3} \tag{4}$$

where η is the viscosity of the water, ξ the correlation length, and R the radius of the probe particle. The order of magnitude estimate of τ_i corresponds to 10^{-3} s in our systems. Inspection of Figure 8 shows that the plateau of $\Delta r^2(t)$ extends on both sides of this value. In fact, it was argued previously[5] that the correction factor taking into account the contribution to the compressional deformation was quite small.

Referring back to eq 3, there is also an uncertainty concerning the numerical prefactor in front of $k_BT/R^2\delta$. From the relationship established by Xu et al.[21] between $\langle \Delta r^2(t) \rangle$ and the creep compliance of the gel, the prefactor in eq 3 should be $1/\pi$.

Taking into account these remarks, the comparison between the different techniques will concern mainly the evolution of μ as determined by eq 3 with parameters of the gel such as the concentration and the cross-linking ratio.

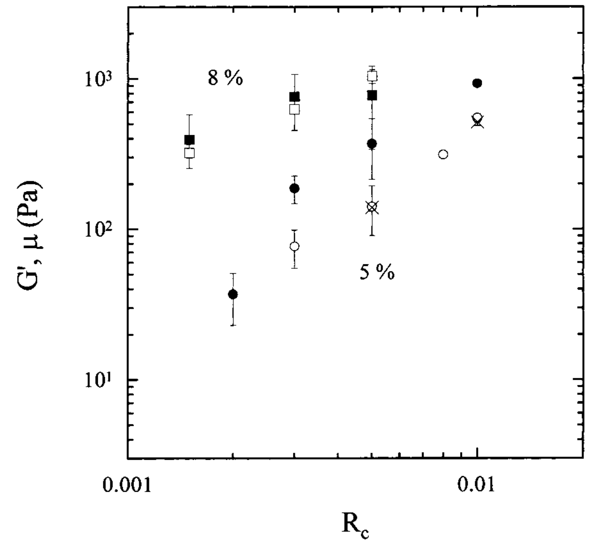

Figure 11. Comparison of microscopic shear modulus μ with macroscopic storage modulus G' of PVA gel: open circles, macroscopic (without latex), $C_p = 5\%$; crosses, macroscopic (with latex), $C_p = 5\%$; filled circles, microscopic, $C_p = 5\%$; open squares, macroscopic (without latex), $C_p = 8\%$; closed squares, microscopic, $C_p = 8\%$.

Figure 11 shows the comparison between the modulus μ of PVA gels and the macroscopic value G' measured by classical rheometry for gels at two concentrations and various cross-linking ratios. The values of G' have been taken at the highest frequency investigated ($\omega = 92$ Hz). This frequency is still lower than the range of frequencies probed by DWS ($\omega \sim 1000$ Hz). One observes a good

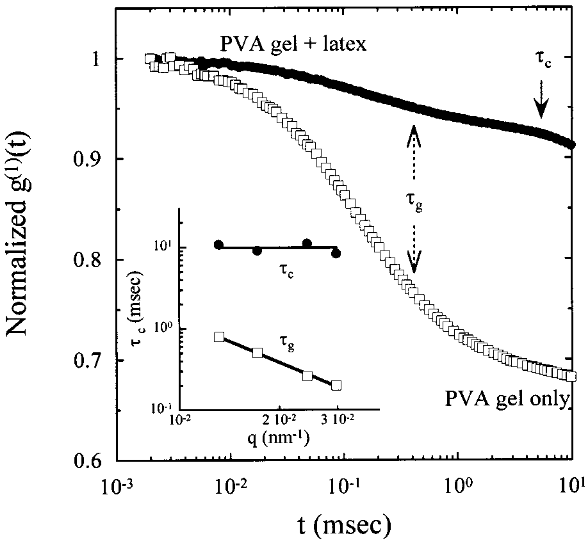

Figure 12. Dynamic structure factor $g^{(1)}(t)$ of PVA gels ($C_p = 2\%$, $R_c = 0.01$) with/without latex. Inset: characteristic times of the Brownian cage τ_c and of the concentration fluctuations of the gel τ_g as a function of q. Latex diameter: 107 nm. Latex concentration: 0.01%.

agreement between the two sets of data for gels with $C_p = 8\%$. For these gels the increase of the modulus with cross-linking ratio is slightly less than the linear dependence expected from the rubber elasticity theory.

For the gels with $C_p = 5\%$ the agreement between G' and μ is not as satisfactory. This might be due to an enhanced frequency dependence of the modulus as the polymer concentration and/or the cross-linking ratio are lower. The large variation of G' and μ with the cross-linking ratio has already been reported for other systems,[23] and it is assumed to be the consequence of formation of dangling chains at low cross-linking ratio and trapped entanglements at high cross-linking ratio.

It must be also remarked that these effects are much more sensitive on the shear modulus than in the swelling equilibrium concentration, as shown in the inset of Figure 5. Experiments conducted in gels containing controlled amount of dangling chains have shown that the modulus drops rapidly when this amount is increased, whereas the swelling equilibrium concentration remains almost unaffected.[24]

One other thing we should emphasize here is that the addition of latex particles at a volume fraction of 1% for DWS measurements does not change the value of the macroscopic modulus as shown in Figure 11.

Finally, we discuss the comparison of cage dynamics in DWS and DLS experiment. It is possible to investigate the cage dynamics by DLS when the characteristic length of the cage is large enough, that is, for gels with low cross-linking ratio and/or low polymer concentration. Also, the size of the probe particle must be small. Figure 12 shows the dynamic structure factor of the latex (0.1 μm, 0.01%) dispersed in PVA gel. The decay function is bimodal, the fluctuations of polymer concentration and the motion of confined particles being observed simultaneously. The slow relaxation corresponds to the cage dynamics, whereas the fast one has the same characteristic time as the bare gel as shown in the Figure 12. The characteristic time of the cage is independent of q, while the fluctuations of the gel are diffusive as inferred from the q^2 dependence of the relaxation time (cf. inset). The fluctuating and frozen-in components of light scattered by both the latex and gel were determined by fitting a two-component exponential function. The fraction of the frozen-in intensity scattered by the latex A_G can be related to δ according to

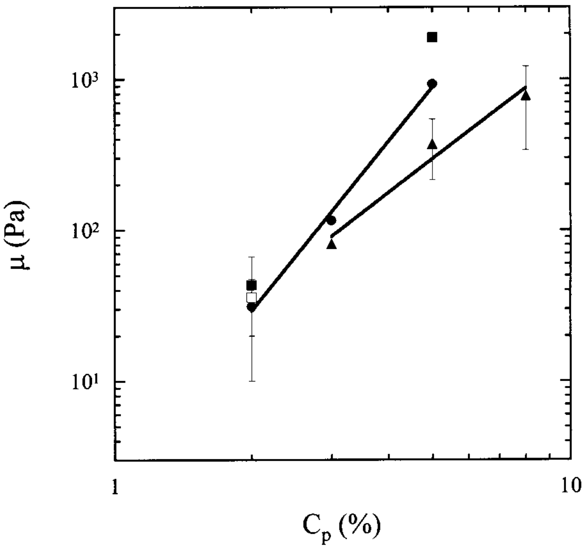

Figure 13. PVA concentration dependences of the local shear modulus μ determined by DWS and DLS: filled circles, $R_c = 0.01$ probed by DWS of 535 nm latex; filled squares, $R_c = 0.01$ probed by DWS of 107 nm latex; open rectangles, $R_c = 0.01$ probed by DLS of 107 nm latex; filled triangles, $R_c = 0.005$ probed by DWS of 535 nm latex.

$$A_G = \exp(-q^2\delta^2) \tag{5}$$

From the value of δ, the shear modulus μ was determined by DLS and compared with that obtained by DWS. Figure 13 shows the variation of the shear modulus μ as a function of PVA concentration. The comparison between the values of μ for a PVA gel with $C_p = 2\%$ and $R_c = 0.01$ measured by DLS and those determined by DWS indicates that the two methods are equivalent and that the addition of concentrated latex to the gel does not affect the modulus.

The PVA concentration dependence of the shear modulus shown in Figure 13 can be fitted by a power law with an exponent 3.7 for $R_c = 0.01$ and 2.3 for $R_c = 0.005$. Theoretically, this exponent is predicted to be 1. This discrepancy could be due to reduced values of μ when the gel is prepared at low concentration close to gelation threshold (about 1.8%). Similar results are reported for system measurements by particle tracking in polyacrylamide gels.[7]

The effect of the particle radius on the value measured of the shear modulus is shown in Figure 13. For a PVA gel with $R_c = 0.001$, the value of μ determined by using 107 nm latex particles is about twice that obtained with 535 nm particles. A possible explanation is that higher frequencies are probed when the particles are smaller according to eq 4. The characteristic frequency ($1/\tau_i$) is expected to be 25 times larger for 107 nm particles than for 535 nm particles, and this might increase the observed shear modulus.

Conclusion

The motion of probe particles an aqueous PVA solutions and chemically cross-linked gels has been investigated in a large time range by DWS. The time dependence of the mean-square displacement $\langle \Delta r^2(t) \rangle$ of the particles was studied as a function of the amount of cross-linker in the system, allowing to probe the evolution of the dynamics of the system when passing from linear chains to branched chains to permanent gels.

At long time the particle motion is diffusive for linear or weakly branched chains, subdiffusive for highly branched chains, and caged for gels.

The behavior of $\langle \Delta r^2(t) \rangle$ at short time is about the same for highly cross-linked gels close to their swelling equilibrium condition and solutions of linear and branched polymers whereas the mean-square displacement is enhanced in gels with low cross-linking ratio. This indicates an effect of the cross-linking ratio on the high-frequency viscoelasticity of the system.

From the long-time plateau of $\langle \Delta r^2(t) \rangle$ in DWS experiments the shear modulus of gels was determined and found to be in reasonable agreement with the measurements by DLS and classical rheometry.

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