

Quasielastic Light Scattering Measurements of Self-Diffusion and Mutual Diffusion in Gelatin Solutions and Gels

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There has been considerable interest in comparing the mutual diffusion coefficients, measured by quasielastic light scattering, for a concentrated or semidilute uncross-linked polymer solution and for a cross-linked gel having identical or nearly identical chemical structure and the same polymer concentration. In several cases, the mutual diffusion coefficients have been found to be the same (JARRY and PATTERSON 1982) or closely similar (MUNCH, et al. 1977a, 1977b). In the study reported here, quasielastic light scattering measurements have been made on semidilute solutions of gelatin and the corresponding gels that are formed from these solutions at lower temperatures. Although gelatin is in a sense a poor choice of polymer because of its complex structure, uncertain gelation mechanism, and broad molecular weight distribution, it behaves above the gel temperature as a random coil polymer (VEIS 1964) and the viscoelasticity of its gels corresponds to that of a network of flexible strands (LAURENT, et al. 1980). In the present study, it has the unique advantage that viscoelastic measurements (LAURENT, et al. 1980) of the same gels have previously provided values of the translatory monomeric friction coefficient ζ_0 as well as accurate values of the macroscopic shear modulus G , so the relation between scattering and mechanical measurements can be examined. From the scattering measurements on solutions above the gel temperature, the mutual diffusion coefficient D_c is determined as well as a much smaller diffusion coefficient D_2 which can be identified as the self-diffusion coefficient of the polymer. For the gels, only D_c is obtained, and its dependence on temperature and solvent viscosity (varied over a wide range by incorporation of glycerol up to 91% by weight) is examined. Over the range studied, both the friction coefficient ζ_0 and the shear modulus G were previously observed to depend on both these variables (LAURENT, et al. 1980).

EXPERIMENTAL

The gelatin (pigskin), provided by Rousselot S. A., Paris, was the same sample used in the previous investigation of viscoelastic properties (LAURENT, et al. 1980), and characterization data are reported in that publication. The number-average molecular weight (35,000) and intrinsic viscosity (22 ml/g) are relatively low and reflect a substantially degraded sample. From experience with similar gelatins (VEIS 1964), the molecular weight distribution is probably rather broad.

The solvents were water and glycerol-water mixtures containing 60, 73, and 91% glycerol by weight. All the gels were made up to contain 15.0% gelatin by weight; the concentration of the solutions ranged from 2 to 20%.

The concentration in g/cm^3 (c) was calculated by assuming additivity of gelatin and solvent volumes, taking the gelatin density as 1.465 g/cm^3 .

Prior to the quasielastic light scattering measurements, the warm solutions were filtered through Gelman Metricel 0.45μ filters into cylindrical scattering cells (10mm dia.). In experiments above the gel temperature, the samples were held at $35.0 \pm 0.3^\circ\text{C}$, usually for at least two hours prior to the measurements, which were made at the same temperature. In experiments on gels, each sample was kept at 0°C for 5 hours and then equilibrated for 15 ± 2 hours at the desired temperature for the measurements.

The quasielastic light scattering was measured using a 64 channel real time autocorrelator (K7025; Malvern Instruments, Ltd., Malvern, Worcs., U.K.) connected to a commercial goniometer (Malvern RR103) (AMIS, et al, 1981). The autocorrelation function of the scattered incident light from an Argon laser (Lexel 75-.2) at 514.5 nm wavelength was acquired as a function of scattering angle from 30° to 135° with a selected photomultiplier tube (ITT FW 130) operated in a photon counting mode. The addition of a temperature control coil to the goniometer sample holder allowed temperature regulation in the range 5°C to 35°C to better than $\pm 0.2^\circ$. An Apple II microcomputer (Apple Computer, Inc., Cupertino, CA) interfaced to the correlator provided data storage and preliminary analyses. Subsequent detailed fittings to various model functions were performed using nonlinear regression routines on a Harris/7 minicomputer.

The normalized intensity autocorrelation function for heterodyne detection arising from a single diffusive process with the decay constant Γ can be written as (BERNE and PECORA 1976)

$$g^{(2)}(\tau) = G^{(2)}(\tau)/\beta = 1 + Ae^{-\Gamma\tau} \quad (1)$$

with $\Gamma = D\kappa^2$, where A is an instrument optical constant, D is the diffusion coefficient and κ is the magnitude of the scattering wave vector, defined as $(4\pi n/\lambda_0) \sin(\theta/2)$ with n the refractive index of the medium, λ_0 the incident wavelength in vacuo and θ the scattering angle. $G^{(2)}(\tau)$ is the unnormalized experimental autocorrelation function and the normalization constant β for $g^{(2)}(\tau)$ is chosen as

$$\beta = \lim_{\tau \rightarrow \infty} G^{(2)}(\tau). \quad (2)$$

This described the data for all gel samples, and the heterodyne detection mode was confirmed by observing that there was no change in the measured decay constant when a macroscopic inhomogeneity was deliberately introduced into the scattering volume. Because of the wide range of the solvent viscosity adjusted by the glycerol concentration (0, 60, 73, 91%) at three different temperatures (5, 12, 20°C), the required correlator sample times (or delay times) $\Delta\tau$ ranged from 5000 to $0.5 \mu\text{sec}$ and yielded decay constants Γ from 2 sec^{-1} to $4 \times 10^4 \text{ sec}^{-1}$. For sample times below $1 \mu\text{sec}$ it was often necessary to delete 1 to 3 points at the beginning of the autocorrelation function due to errors in the detection electronics. The calculated decay constants gave linear plots against κ^2 .

For the gelatin samples at temperatures above the melting point, the quasielastic light scattering was more complicated and required a different scheme of data acquisition and analysis. These experiments performed at

35°C on water solutions of gelatin at concentrations from 0.020 to 0.213 g/cm³ showed two clearly distinguishable decays. Fig. 1 demonstrates this observation. On the upper left quarter of the figure the initial fast decay as acquired by the correlator with a sample time of 2 μsec is shown where $g^{(2)}(\tau)$ settles down to an apparent asymptote in this time scale. In the middle of the figure the time scale changes to show the second decay, displayed in the upper right quarter, which was obtained with 200 μsec as the sample time. Even though these correlation functions were measured at different times, it was possible to maintain the experimental conditions such that they can be so spliced together. The analyses of the two decays are effected differently. For the fast one we use Eq. 1, for it is assumed to come by heterodyne detection. For the slow one, however, homodyne detection is more likely, so that the normalized autocorrelation function is

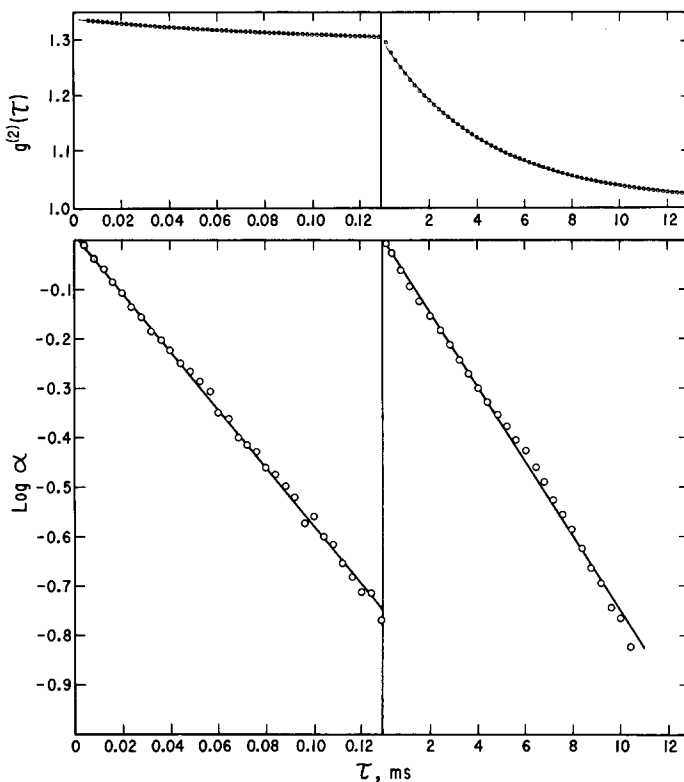


FIG. 1. Top: plot of normalized autocorrelation function with two time scales for a solution at 35°C., $c = 0.103 \text{ g/cm}^3$. Sample time 2 μs at left, 200 μs at right. Each curve is a single exponential fit. Bottom: semilogarithmic plots of same data with α defined by Eqs. 4 and 5.

expressed as (BERNE and PECORA 1976)

$$g^{(2)}(\tau) = G^{(2)}(\tau)/\beta' = 1 + A'e^{-2\Gamma\tau} \quad (3)$$

where A' and β' have the analogous meaning as in Eq. 1. In the lower half of Fig. 1, we display the results of these analyses by plotting $\log \alpha$ against τ where

$$\alpha \equiv \{[G^{(2)}(\tau)/\beta] - 1\}/A \quad (\text{fast decay}) \quad (4)$$

and

$$\alpha \equiv \{[G^{(2)}(\tau)/\beta'] - 1\}^{1/2}/\sqrt{A'} \quad (\text{slow decay}) \quad (5)$$

for the left and right quarters respectively. Thus the slopes of the lower plots represent the decay constant of the fast one, Γ_f , and that of the slow one, Γ_s , respectively.

When a pair of scattering diffusive processes is as well separated in time scale as here, the fast process is generally detected by heterodyne signal whereas the slow process is by homodyne signal provided the fast and slow processes give rise to the weak and strong scatterings respectively. This conclusion has been confirmed by studies of scattering from mixtures of polystyrene latex particles (AMIS 1981).

As an additional check on the determination of the slow decay constants, the second order cumulant analyses (KOPPEL 1972) of the slow decays were also performed. In all the scattering experiments, the incident laser light was polarized with its electric vector perpendicular to the scattering plane (vertical) and no depolarized scattering was observed.

Steady-flow viscosities of the aqueous solutions (no glycerol) were measured at 35°C by capillary viscometry. Further experimental details are given elsewhere (AMIS, et al. 1982).

RESULTS

Solutions Above Melting Temperature. Measurements above the melting temperature were made only on aqueous solutions containing no glycerol. For the fast decay observed with short sample times in these solutions, plots of Γ_f against κ^2 were linear within experimental error. Similar results were obtained for the slow decay observed with long sample times.

The diffusion coefficients calculated from the plots of Γ_f vs. κ^2 and Γ_s vs. κ^2 , identified as D_c and D_2 for the fast and slow mechanisms respectively, are plotted logarithmically against gelatin concentration in Fig. 2. The fast diffusion coefficient, D_c , increases with concentration, approximately with the 0.3 power, from 328×10^{-9} to 638×10^{-9} cm²/sec. This is consistent with the behavior of the mutual diffusion coefficient in a good solvent, where the observed exponent is near zero at very low concentrations, and increases with concentration and/or molecular weight to reach values as high as 0.7 to 0.8 (MUNCH, et al. 1977, NYSTRÖM and ROOTS 1980, SUNDERLÖF 1979). Other reasons for identifying this mechanism with the mutual diffusion coefficient D_c will be given below,

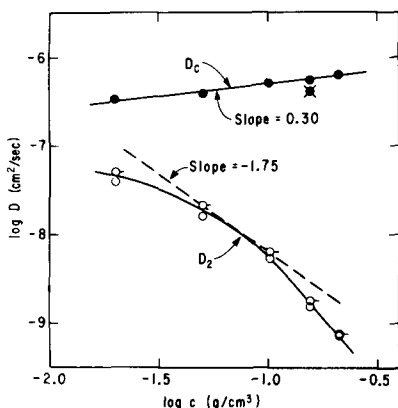


FIG. 2. Logarithmic plot of D_c (fast) and D_2 (slow) against gelatin concentration for solutions at 35°C. Points without pips, single exponential fit to autocorrelation function; with pips, second-order cumulant model function. Point with cross, gel at 20°C. Open circles, homodyne assumed; black circles, heterodyne assumed.

The slow diffusion coefficient, D_2 , decreases sharply with increasing concentration, from 40×10^{-9} to 0.7×10^{-9} cm²/sec. This is the behavior expected for the self-diffusion coefficient of the polymer; very similar curves for the self-diffusion of polystyrene in benzene solutions, measured by forced Rayleigh scattering, have been reported by HERVET, et al. (1979) and LÉGER, et al. (1981). At high concentration and/or molecular weight, where entanglement is present, D_2 was found by them to be proportional to $c^{-1.75}$. A line with the slope of -1.75 is drawn tangent to our curve. Other reasons for identifying this with the polymer self-diffusion coefficient D_2 will be given below. (The notation follows the convention that D_1 and D_2 are the self-diffusion coefficients of solvent and polymer respectively.) It would be expected that D_c and D_2 would converge at infinite dilution to a common value D_0 ; a plot with a linear c scale is consistent with this expectation.

In one qualitative experiment on gelation kinetics, a 15% solution in water was quickly cooled from 35° to 20° and measurements were made repeatedly over a period of two hours. At first, both slow and fast decays were observed, but the former disappeared within ten to fifteen minutes. (A much longer time is required for the modulus of rigidity G to approach a constant value.)

Gels. In the gels, the slow mechanism associated with D_2 does not exist, consistent with the expectation that there can be no self-diffusion of the polymer in a cross-linked structure; only D_c is observed. Values of D_c for the gels are listed in Table 1 together with the solvent viscosities at the respective temperatures.

In water (zero glycerol), D_c appears to decrease slightly with increasing temperature, but this is believed to be an artifact of experimental uncertainty. The average value is 427×10^{-9} cm²/sec, which is somewhat smaller than the value of the corresponding solution at 35°C, 552×10^{-9} cm²/sec. However, it is clear that gelation has affected D_c very little. The point for the gel is included in Fig. 2. This conclusion is similar to that reached for gel networks of a polyepoxide (JARRY and PATTERSON 1982), polystyrene (MUNCH, et al. 1977a) and poly(dimethyl

Table 1. Data for Gels with 15% Gelatin by Weight

Temp. °C	% Glycerol	c g/cm ³	η_s poise	D_c cm ² /sec x 10 ⁹
5	0	0.158	0.0152	436
	60	0.180	0.229	20.6
	73	0.185	0.821	4.50
	91	0.191	8.51	0.28
12	0	0.157	0.0124	432
	60	0.179	0.155	30.0
	73	0.184	0.479	6.76
20	0	0.147	0.0100	412
	60	0.179	0.108	38.8
	73	0.184	0.302	10.6

siloxane) (MUNCH, et al. 1977b), although for the latter two D_c appeared to be slightly higher in the networks than in the corresponding solutions.

A logarithmic plot (not shown) of D_c for the gels against the solvent viscosity η_s for all temperatures and glycerol concentrations, covering a range of three orders of magnitude, is linear with a slope of -1.05; it is evident that within experimental error D_c and η_s are inversely proportional.

DISCUSSION

For a free-draining polymer molecule without entanglements, the self-diffusion coefficient should be given by

$$D_2 = kT/P\zeta_0 \quad (6)$$

where P is the degree of polymerization and ζ_0 is the friction coefficient per monomer unit of the polymer moving through its total environment. In a 15% aqueous solution, the product $c[\eta]$ is 3.4, which is high enough for coil overlap to screen hydrodynamic interaction and to provide free draining behavior (FERRY 1980, p. 213). Although screening of hydrodynamic interaction has been recently confused with entangling, it should be emphasized that the two phenomena are distinct, and the onset of the latter (entanglement regime) occurs at higher concentrations and/or molecular weights than that of the former (semidilute regime) (FERRY 1980, p. 213). The degree of entanglement here should be slight if any; there is no estimate of the entanglement spacing M_e of a polypeptide chain, but a representative value of 5000 for the undiluted polymer would correspond at 15% concentration to $M_e = 47,000$, which is above the total average molecular weight. Thus Eq. 6 should be applicable. The value of ζ_0 in a 15% gel has been determined from viscoelastic measurements (LAURENT, et al. 1980) (by matching to the Rouse theory with assumption of free draining) as 3.0×10^{-8} dyn-sec/cm at 12°C, and it was evident from the analysis of those data that ζ_0 was proportional to η_s ; so it can be adjusted (from the η_s data in Table 1) to 1.74×10^{-8} at 35°C; it should not be changed by melting the

cross-links. The calculation must be very crude because of the broad molecular weight distribution, but if P is taken as 350 ($\bar{M}_n = 35,000$, $M_0 = 100$ from average of amino acids (VEIS 1964)) we obtain from Eq. 6 $D_2 = 6.9 \times 10^{-9}$ cm²/sec. The agreement with the observed value of 1.6×10^{-9} is quite reasonable in view of the fact that the diffusion is strongly weighted by high molecular weight species and the number-average is too small an average to use in this approximate calculation; the z average would be more appropriate. The result supports the identification of D_2 as the self-diffusion coefficient. To the best of our knowledge, this is the first instance of the self-diffusion coefficient of a polymer chain in semidilute solution being extracted from quasielastic light scattering measurements.

Further discussion of the mutual diffusion coefficient, and of the osmotic compression modulus calculated from the mutual diffusion coefficient to the gel shear modulus of elasticity, will be presented elsewhere (AMIS, et al. 1982).

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