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Laser Light Scattering from Mechanically Excited Gels

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ABSTRACT: Laser inelastic light scattering was used to study gels which had been polymerized in light-scattering cuvettes. A sweep generator, connected to an audio frequency transducer, was used to excite mechanical oscillations in the samples. Discrete resonant peaks were noted in the voltage spectra of the scattered light at frequencies which are related to the dimensions of the cuvettes and the mechanical rigidity of the specimens. The temperature and concentration dependences of the shear modulus of elasticity were examined for several polyacrylamide gels. The data fit the relationship $\mu \sim Tc^{\alpha}$, where the exponent α has the value $\alpha \simeq 2.95$. Complementary measurements also were made when the gels were not subjected to external mechanical excitation, and the temperature and concentration dependence of the resulting Lorentzian line widths were determined.

We recently showed that laser light scattering can be used to determine elastic moduli of soft amorphous gels.[1] Standing displacement waves easily can be established within samples of such materials, as is indicated by the fact that oscillations readily appear in measured photon autocorrelation functions. The frequencies of the oscillations have been shown to depend on the dimensions of the containers and on the elastic properties of the test substance,[1] suggesting that the light-scattering cuvettes act as mechanical resonant cavities which select and enhance density fluctuations of particular wavelengths. We found that such standing waves can be sustained by weak, low-frequency, mechanical vibrations whose frequencies are not necessarily close to those of the resonant modes.

Most of our former work pertained to low-density agarose gels which move when gently shaken, and which slip easily along the sides of the light-scattering cuvettes within which they are contained.[1] In this paper, however, we report observations on cross-linked polyacrylamide samples of various compositions. Not only are these gels much stiffer than the extended agarose networks which previously were studied, but boundary conditions are different in that, when polymerized in situ, polyacrylamide gels adhere strongly to the walls of the glass cuvettes in which they are contained.

It is very difficult to observe spontaneous standing waves in such stiff, strongly adherent materials. However, when the samples are driven by an externally applied acoustic mechanical field, resonances in the self-beat light-scattering spectrum are readily apparent and measures of elasticity can be obtained. The parameter which can be extracted in this case is the shear modulus of elasticity.[2,3] Evidence to support this conclusion is presented below, where we show that values determined in the present measurements are similar to those obtained by other techniques. Moreover, changes in deduced values of moduli, which occur when temperature is varied, are shown to be in accordance with this conclusion.

Several salient aspects of the theory underlying these measurements are summarized in the next section (Techniques), where we also describe experimental procedures. In the Resonance Measurements section we present data relating to the concentration and temperature dependence of the moduli. Results of complementary line width and intensity measurements are given in the Line Width Measurements (augmenting recent work of Tanaka et al.[4]), and a short discussion appears in the Remarks section.

Techniques

a. Theory (Summary). A theoretical analysis of the cavity resonance techniques which are used in these experiments is presented in detail in ref 2. The model adopted therein relates fluctuations in the diffraction pattern of scattered light to the reorganization of a polymer lattice which occurs when a macroscopic displacement wave passes through an isotropic gel. The details of the diffraction pattern cannot be specified unless the microscopic structure of the gel has been determined, but we nevertheless know that the scattering pattern will vary with the same temporal periodicity as will macroscopic displacements which might be induced in the material. Gels having high polymer concentration may, to first order, be spatially homogeneous on a length scale comparable to the wavelength of light, but scattering from imperfections such as domain boundaries and dust will produce a weak, time-varying, diffraction pattern. Moreover, if the polymer concentration is sufficiently low (as, e.g., in the agarose and fibrin gels which we have reported on elsewhere[1,5]), spatial heterogeneities intrinsic to the gel structure itself will exist on a length scale of the order of that of light, and a larger amount of scattering will be discerned.

To describe macroscopic motions we assume[2] that the following modified classical elasticity equations can be used:

$$\rho \frac{\partial^2 U_{x_i}}{\partial t^2} = \mu \nabla^2 U_{x_i} + (\lambda + \mu) \frac{\partial}{\partial x_i} (\nabla \cdot \mathbf{U}) + \varphi_{x_i} - \zeta \left(\frac{\partial U_{x_i}}{\partial t} - V_{x_i} \right) + \eta \nabla^2 \frac{\partial U_{x_i}}{\partial t} + (\chi + \eta) \frac{\partial}{\partial x_i} \left(\nabla \cdot \frac{\partial U}{\partial t} \right) \quad (1)$$

In these equations $\mathbf{U}(\mathbf{r},t) \equiv (U_x,U_y,U_z)$ are the components of the displacement vector, ρ is the material density, λ and

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μ are the Lamê coefficients, and χ and η are analogues of viscosity coefficients which account for internal energy dissipation throughout the extended gel.[6] When eq 1 is applied to motions of the polymer lattice alone, ζ then represents the friction between polymer strands and surrounding solvent fluid, $\mathbf{v}(\mathbf{r},t)$ represents local motions of that fluid, and φ pertains to possible external body forces. However, when the polymer matrix and the solvent are considered to move together, $\mathbf{v}(\mathbf{r},t)$ and ζ are identically zero, and the quantities ρ, μ, λ, χ, and η pertain to the entire gel.

In ref 2, we solve eq 1 subject to two idealized sets of boundary conditions. Both consider that a gel be formed in a rectangular cuvette, but one relates to the case where the sample slips easily along the cuvette walls and the other pertains to the situation where the specimen is strongly adherent. In both instances we find that the solution can be expressed as a series of standing displacement waves whose frequencies are given as

$$\omega = Ck_{\alpha\beta\gamma} \tag{2}$$

where C is a sound speed which depends upon the material parameters of the sample. $k_{\alpha\beta\gamma}$ is a wavenumber which can take discrete values according to

$$k_{\alpha\beta\gamma} = \pi\left(\left[\frac{\alpha}{a}\right]^2 + \left[\frac{\beta}{b}\right]^2 + \left[\frac{\gamma}{c}\right]^2\right)^{1/2} \tag{3}$$

where a, b, and c are the dimensions of the cuvette, α and β are integers, and γ is an integer or half-integer. Theoretical analysis of a simplified model in which a gel is driven with mechanical excitation leads to the conclusion[2] that, in the first case (slippery gels), C is the "longitudinal sound speed"

$$C_l = ([\lambda + 2\mu]/\rho)^{1/2} \tag{4a}$$

and, in the second instance (adherent gels), C is the "transverse sound speed"

$$C_{tr} = (\mu/\rho)^{1/2} \tag{4b}$$

The intensities of the standing wave components are proportional to $\{g_0(\nu)\}$, the strengths of the imposed mechanical excitations at frequencies $\{\nu\}$. If ν is close to one of the frequencies given, e.g., by eq 2 and 4b, then the amplitude of the response (assuming the simple excitation model) is given as[2]

$$|U| \simeq \frac{16(\zeta + \eta k^2_{\alpha\beta\gamma})^2\nu^2 g_0}{\pi^2\rho^2\beta\gamma\{[\nu^2 - k^2_{\alpha\beta\gamma}C_{tr}^2]^2 + \nu^2(\zeta + \eta k^2_{\alpha\beta\gamma})^2/\rho^2\}} \tag{5}$$

Thus, resonant behavior is indicated and, since it can be shown that the spectrum of scattered light will be proportional to the square of the quantity given in eq 5, we conclude that a suitable method for detecting the fundamental frequencies of stiff gels would be to drive the gels with an oscillator whose frequency is continually changed.

Such, in essence, is the procedure which we have used. An example of a typical measured amplitude spectrum is shown in Figure 1. From eq 5 one can show that the half-width of the resonance is given by $(\zeta + \eta k^2_{\alpha\beta\gamma})/\rho$ (see ref 2). However, we recall that ζ represents friction between solvent and polymer lattice, and if lattice movements essentially are always coordinated with those of the solvent, this dissipative term then can be set equal to zero in eq 1 and in subsequent expressions. Since for polyacrylamide and similar materials ζ is of the order of 10^{10} dyn s/cm[4],[4,7] an immediate conclusion is that the data shown in Figure 1 must relate to the collective motion of the entire gel consisting of both polymer and solvent, rather than to the motion of the polymer lattice alone (otherwise the resonance would be too broad to be discernible).

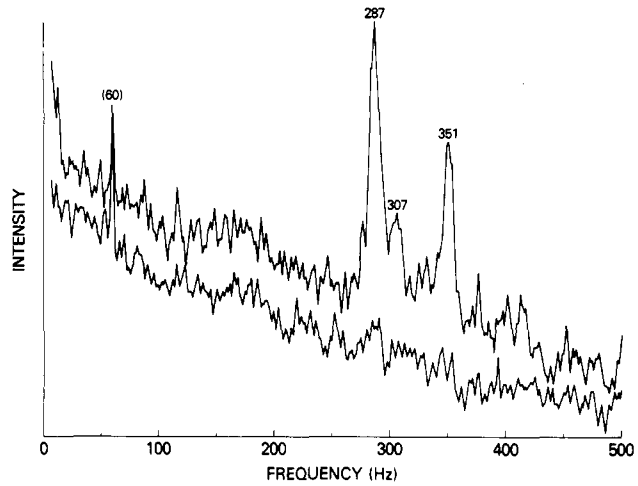

Figure 1. Typical spectrum of light scattered from a moderately stiff gel exposed to an external sound field. The top record was obtained while the sample was excited by a signal obtained from a sweep generator which was oscillating over the range 161 to 341 Hz; prominent resonances are seen to occur at 287, 307, and 351 Hz. The bottom tracing was obtained while the generator was sweeping over a range of 48 to 102 Hz; except for the spurious 60-Hz signal, no resonances are discernible. The sample was 7.5% polyacrylamide in a 1 × 1 × 4 cm cuvette, $T \simeq 4.8$ °C, scattering angle $\simeq 22°$.

Because the motions of an adherent gel are coordinated with those of the rigid walls of the cuvette, the mode structure for a displacement in the $\hat{x}$ direction $U_x(\mathbf{r},t)$ has the form[2] $U_x \sim \sin(\beta\pi y/b)\sin(\gamma\pi z/c)$ [i.e., $\alpha = 0$]. However, since shear modes in a compound gel are stimulated by twisting movements of the cuvette, considerations of symmetry imply that β is an even integer. Thus, the lowest order prominent spectral peak is located at a frequency ν_0 given by[2]

$$\nu_0 = k_{\alpha\beta\gamma}C_{tr} = k_{\alpha\beta\gamma}(\mu/\rho)^{1/2} \tag{6}$$

where the coefficients $\{\alpha,\beta,\gamma\}$ are[2,3] $[0,2,{}^1/_2]$.

b. Experimental Apparatus. Sample Preparation. The spectrometer employs a Coherent Radiation CR-2 Argon ion laser as a source (4880 Å) and utilizes an optical arrangement which has been described by Shaya et al.[8] An EMI 9840B photomultiplier tube is used as the detector, the output of which is passed through a wide-band amplifier (Ortec 4660) and then to a Nicolet UA500B real-time spectrum analyzer.[1] The principal modification here is that an external source of mechanical vibration is used to excite the specimen. A schematic diagram is shown in Figure 2. We use the amplified output of a sweep generator (Wavetek, Model 114) to drive a simple audio speaker coupled to the light-scattering apparatus with a block of polystyrene, and we thus can vary the frequency of the mechanical field continuously over a predetermined range. (The sweep is calibrated by connecting the output of the oscillator directly to the spectrum analyzer, setting the frequency range, and choosing a sweep rate which is sufficiently slow that the resolved bandwidth of the moving oscillation is narrower than that of the resonance lines which are being detected.)

Polyacrylamide samples were prepared by polymerizing acrylamide and N,N'-methylenebis(acrylamide), with ammonium persulfate as an initiator, and N,N,N',N'-tetramethylethylenediamine ("TEMED") as a catalyst (BioRad Laboratories). The weight ratio of acrylamide to

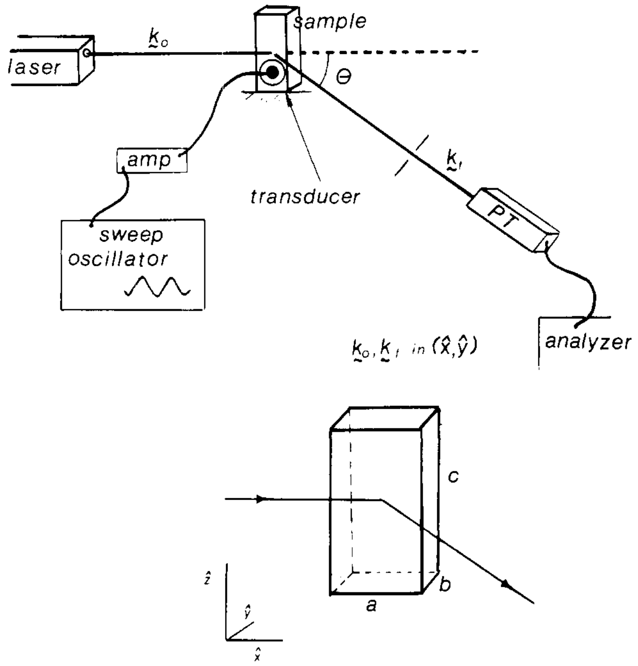

Figure 2. Scheme used for probing mechanically induced displacement waves. The long axis of the cuvette usually is positioned perpendicularly to the Bragg scattering vector.

Table I
Amounts of Each Component (mL) in the Polyacrylamide Gels Used in These Experiments

% polyacrylamide	acrylamide soln[a]	ammonium persulfate soln[b]	water	TEMED
2.50	1.67	0.35	17.97	0.01
3.75	2.50	0.27	17.13	0.01
5.00	3.33	0.20	16.46	0.01
6.25	4.17	0.18	15.64	0.01
7.50	5.00	0.15	14.84	0.01

[a] 15.0 g of acrylamide plus 0.4 g of *N,N*-methylethylenebis(acrylamide) in a total volume of 50 mL of water.
[b] 0.1 g of ammonium persulfate per mL of water.

bis(acrylamide) molecules was 37.5:1 (i.e., a molecular ratio of 75:1). The concentration of TEMED was kept constant at 0.05%, but the acrylamide and persulfate concentrations were varied (see Table I). By a gel of, e.g., 5% polyacrylamide, we mean that the concentration of acrylamide monomer was 0.05 g in a total gel volume of 1.0 mL. Samples were polymerized directly in the cuvettes and allowed to stand at room temperature for at least 24 h before being placed in the spectrometer. All samples reported on in these experiments were formed to a height of 4 cm in rectangular cuvettes having a cross section of 1 × 1 cm.

Resonance Measurements

The above described light-scattering scheme was used to measure the rigidity of various polyacrylamide samples. Obvious resonances in photocurrent were noted as the frequency of the external mechanical field was changed. In the example shown in Figure 1 the principal resonance occurs at the value $\nu_0 = 287$ Hz, but the locations of the peaks change when the temperature or polymer concentration is altered. After initial determination of the resonance positions, the sweep range is restricted in order to maximize efficiency of data collection (see figure caption).

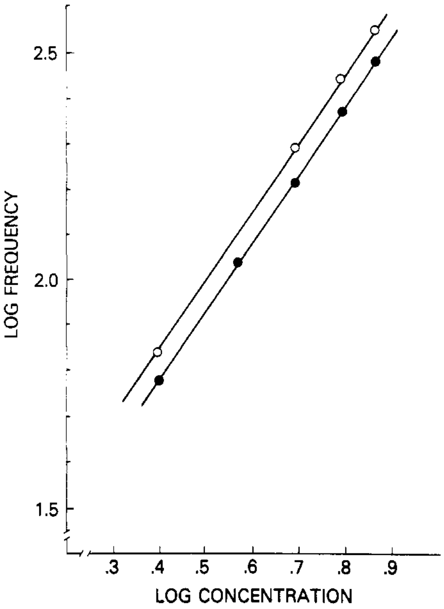

Figure 3. Location of resonance maxima as a function of polyacrylamide concentration (g/cm^3), plotted as log (ν) vs. log (% polymer). The polymer concentrations were varied over a range of 2.5 to 7.5% (see Table I). Correspondingly, the lowest prominent peaks, occurring at frequencies ν_{200} (closed circles), varied over a range of 59 to 302 Hz ($T \simeq 20$ °C). The location of higher order resonances shifted in a similar manner, as is exemplified by the frequencies of the (2,0,4) peak (open circles). (The indices (p,q,n) correspond to $\{\alpha,\beta,\gamma\}$ in eq 3, where $\alpha = p$, $\beta = q$, $\gamma = n + {}^1/_2$ (see ref 2).)

Consideration of resonance widths leads to the conclusion that our mechanical excitation light-scattering scheme measures the rigidity of bulk material, rather than moduli of the lattice alone (see discussion following eq 5). Since boundary interactions for polyacrylamide seem to approximate those of a previously analyzed model of adherent gels, we conclude that the data acquired in this study provide measures of the shear modulus (see eq 6 and 4b), rather than of the compressibility modulus (eq 4a).[2,3] We also note that resonances corresponding to the compressibility modulus of the gel would occur at much higher frequencies because of the incompressibility of the solvent phase.[2] (To a first approximation the moduli of a compound material are the sums of the individual moduli of the solvent and of the polymer lattice.)

Positions of resonance peaks are found to vary markedly as the polymer concentration is changed. Some results are shown in Figure 3. The standing wave frequencies generally[2,3] can take values $\{\omega_{100},\omega_{101},\omega_{102},\omega_{110},\ldots\}$ where ω_{100} designates the resonance of lowest frequency, ω_{101} refers to the next higher order resonance, etc.; however, for shear modes excited in a cuvette having fixed rigid walls, we expect that the indices will be even valued. As in the case of agarose[1] and other gels, we have observed that resonance frequencies for polyacrylamide samples vary with cuvette dimensions according to eq 3.

The shear modulus can be calculated from eq 6, with the value of the density ρ to be that of the compound gel. The latter was measured for differing polymer concentrations and found to be essentially constant over the range shown above. (Although the gels contracted by a few percent, the effect was approximately the same for each sample.) Thus, from the data given in Figure 3, we deduce that μ varies as $\mu \sim c^\alpha$, where $\alpha \simeq 2.95 \pm 0.06$.[22] The latter is in close agreement with a recent theoretical prediction by Daoud and Jannick[9] which indicates that the exponent should have the value $\alpha \simeq 3$. Hecht and Geissler[10] have

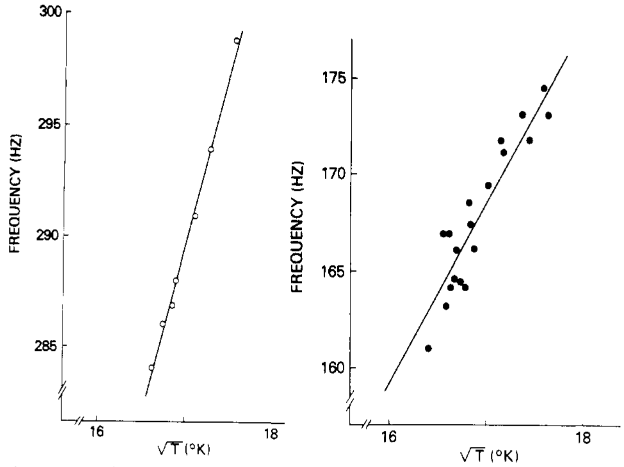

Figure 4. Temperature dependence of the ν_{200} resonance. (a, left) Polyacrylamide concentration $c = 7.5\%$. (b, right) Polyacrylamide concentration $c = 5\%$. The solid lines which have been fitted to the data extrapolate to zero with absolute temperature. From eq 2 and 4, the temperature dependence of the modulus thus is seen to be $\mu \sim T$.

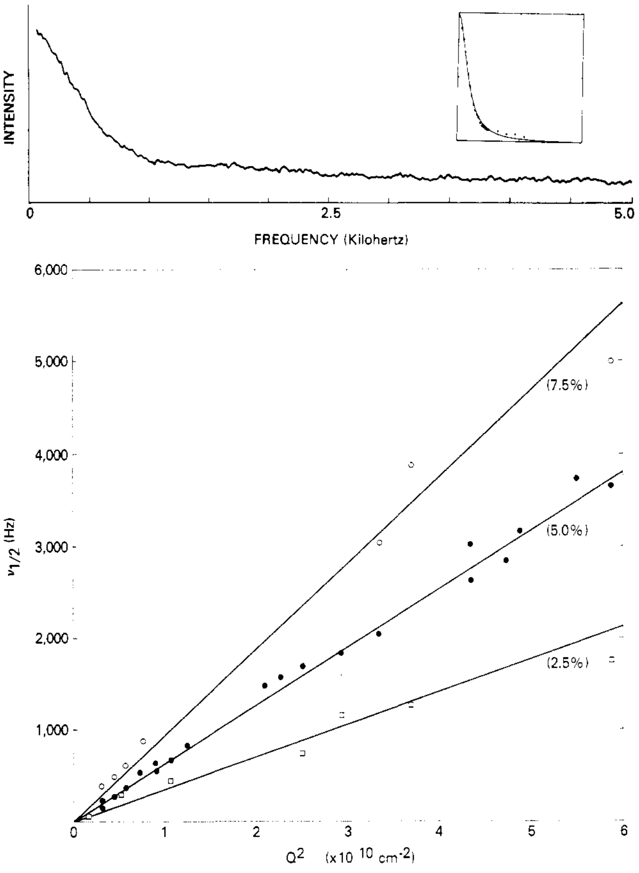

Figure 5. (a, top) Typical spectrum of light scattered from a sample when not subjected to extraneous mechanical perturbations. The inset shows a Lorentzian fit to selected data points. Gel concentration 6.25%; scattering angle $\simeq$ 22°; $T = 20$ °C. (b, bottom) Half-width at half-height, $\nu_{1/2}$, as related to the magnitude of the Bragg scattering vector $Q = 4\pi n\lambda^{-1} \sin \Theta/2$. (Numbers in parentheses indicate polymer concentration.

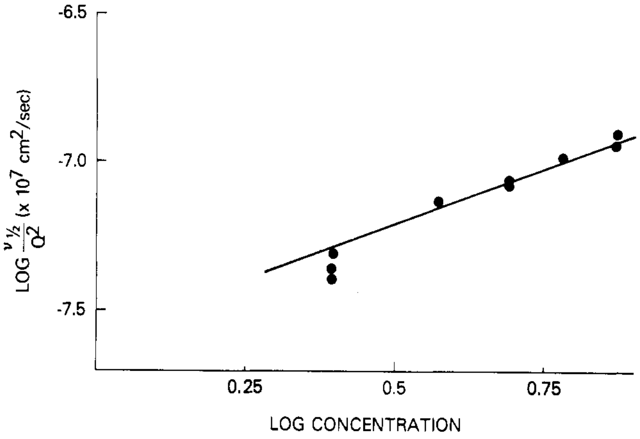

Figure 6. Log–log plot of the concentration dependence of Γ/Q^2 (scattering angle = 22°; $T \simeq 20$ °C). The line has a slope of 0.75, in accordance with a theoretical prediction derived by de Gennes.[14]

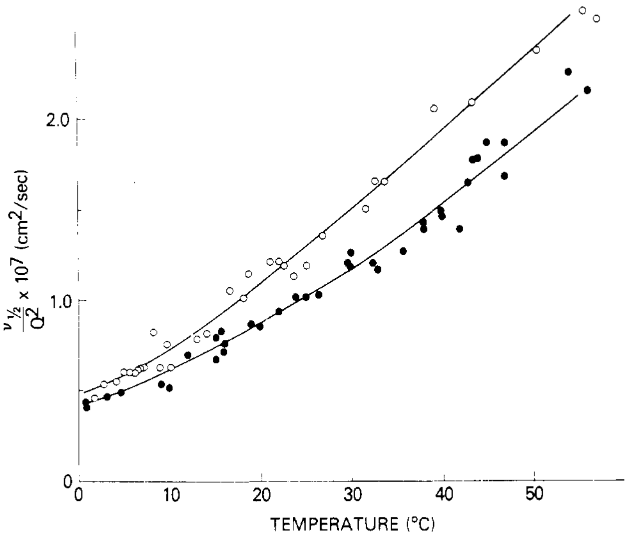

Figure 7. Temperature dependence of the diffusion coefficient. The top curve pertains to a 7.5% polyacrylamide sample and the lower curve is data for a 5% gel.

observed a similar relationship in light-scattering studies of concentrated polystyrene solutions ($2.85 < \alpha < 3$) and examination of results of a study by Belkebir-Mrani et al. regarding the compressional moduli of swollen polystyrene networks (presented in ref 11) leads us to conclude that those data also can be interpreted as substantiating the notion that α is close to a value of 2.9–3.0. Our previously acquired data on agarose[1] indicate that for that material also the exponent is given as $\alpha \simeq 3$.[22]

Additional confirmation of the notion that we here measure the shear modulus μ results from studies on the temperature dependence of the resonant frequencies. Numerous theories[9,12-14] predict that μ should vary directly with absolute temperature, in which case eq 6 implies $\nu_0 \propto T^{1/2}$. In Figure 4 we present results of measurements of studies performed to test this relationship. Because the modulus is a strongly increasing function of concentration, $\mathrm{d}\mu/\mathrm{d}T$ is correspondingly greater, and the best frequency resolution is achieved for the stiffest gels. Figure 4a indicates that data for a 7.5% sample are in very satisfactory agreement with the theoretically predicted $T^{1/2}$ dependence; in Figure 4b we show corresponding results for a 5.0% polyacrylamide sample, for which somewhat greater variability is noted. The lines which have been fitted to the data points extrapolate to zero with decreasing temperature. Furthermore, the slope of the line drawn through points in Figure 4b is consistent with data given in Figure 3 and, also, with the line determined by points in Figure 4a, indicating that the data satisfy the relationship $\mu \sim Tc^{\alpha}$, where $\alpha = 2.95$.

Line Width Measurements

The scattered light spectrum appears as approximately Lorentzian when the external mechanical field is suppressed. A typical experimental record is shown in Figure

5a, where the abscissa represents the frequency of a Doppler shifted component of the scattered field, and the ordinate is proportional to the amplitude of that component (these amplitudes are proportional to the square root of the power spectrum). Thus, if the autocorrelation function varies as $\exp(-\Gamma t)$, the spectral width $\nu_{1/2}$ (half-width at half-height) here is related to the decay parameter Γ according to $\nu_{1/2} = 3^{1/2}(\Gamma/2\pi)$, where $\nu_{1/2}$ has units of frequency (Hz).

The inset in Figure 5a shows a least-squares fit of a Lorentzian curve to the data, for which the decay parameter has been determined to have the value $\Gamma = 1.54 \times 10^3\ \mathrm{s}^{-1}$. We see that the data indeed can be well fit to a single Lorentzian in this case, but such simple fits generally are better at smaller scattering angles. Tanaka et al.[15] and others[7] have indicated that Γ should vary as the square of the magnitude of the Bragg scattering vector, and we find our data to be in accord (see Figure 5b).

The scaled half-width $\Gamma/\mathbf{Q}^2$ can be related to an effective diffusion coefficient, given as[15]

$$D \equiv \Gamma/\mathbf{Q}^2 = (\lambda + 2\mu)/\zeta = (K + \tfrac{4}{3}G)/\zeta \qquad (7)$$

where ζ is the friction coefficient (see eq 1, above), λ and μ are the Lamé coefficients, K is the compressibility, and G is the shear modulus (identical to μ for an isotropic gel). Figure 6 shows that the half-width varies with changes in polymer concentration. The solid line indicates how D could be fit to a power law as $D \sim c^{\beta}$, with the exponent given as $\beta = 0.75$. Studies by Munch et al.[11] on semidilute polystyrene solutions and swollen block copolymers of styrene and divinylbenzene indicate a value of $\beta \simeq 0.66 \pm 0.03$; similar studies by Adam et al.[16] provide a value $\beta \simeq 0.7 \pm 0.05$.

de Gennes has predicted $D \sim c^{0.75}$ for semidilute polymer solutions formed in "good" solvents.[14] However, these predictions for dilute solutions do not necessarily hold for dense polymer networks, and agreement with results given in Figure 6 may be fortuitous. Since our samples of gel are not at the swelling equilibrium state, we expect strong interactions between overlapping polymer chains, i.e., a situation similar to that of polymers dissolved in poor solvents. Indeed, the exponent value discerned from the rigidity data determined from Figure 3 is close to that which has been predicted for semidilute polymer solutions in poor solvents, but a corresponding prediction for D is that it be a linear function of the concentration.[9,17]

In Figure 7, we show how D varies with temperature. The curves are similar to data previously published by Tanaka et al.[4,15] Note, here, that the ratio of $D_{7.5}$ to $D_{5.0}$ is in agreement with the results shown in Figure 6, over the entire temperature range.

Remarks

The main purpose for undertaking this study was to verify that our resonance light-scattering technique[1] can be used to determine the rigidity of stiff gels. The density and temperature dependences of the data presented in Figures 3 and 4 indeed indicate that such measurements can be accomplished. Further evidence is given in Table II, below, where we compare values of moduli determined in this study with values which have been ascertained by other techniques. Results are in accordance with the notion that we measure the shear modulus of the composite gel, including the solvent.

By combining homodyne line widths with measurements of total scattered intensity, Tanaka et al.[4] have been able to determine the longitudinal sound speeds associated with disturbances of the polymer lattice alone (see, also, Geissler and Hecht[18]). This technique determines the sum of the compressibility and shear moduli in the combination $(K + 4/3\mu)_{\text{lattice}}$. Our measurements are complementary; μ_{lattice}, alone, can be ascertained by subtracting the shear modulus of the solvent from values which are determined by the resonance light-scattering technique for the total gel.

Table II
Comparison of Shear Moduli μ (dyn/cm^2)

% polyacrylamide	mechanical measurements			light scattering[d]
	a	*b*	*c*	
2.5	2.2×10^2	[e]	[f]	3.6×10^3
3.75			1.1×10^4	1.2×10^4
5.0	2.6×10^4	2.65×10^4	2.5×10^4	2.7×10^4
6.25			5.2×10^4	5.3×10^4
7.5			8.4×10^4	8.8×10^4
15.0		1.36×10^5		

[a] Uniaxial compression: Tanaka et al.[15] [b] Unilateral compression: Wun and Carlson.[19] [c] Uniaxial compression: Hecht and Geissler, extrapolated data.[20] [d] This study. [e] Get too soft for . . . measurement. [f] . . . unable to measure because of . . . softness.

We also can obtain an estimate of the internal friction coefficient η. Although based on an approximate and somewhat crude theory, eq 5 implies[2] that the resonance half-width is given as $\eta k^2{}_{0,2,1/2}$. Thus, we find from the lowest order peak in Figure 1 the value $\eta = 5$ dyn s/cm^2.

Additional Note. Hecht and Geissler[20,21] recently have performed light-scattering studies of the elastic moduli of polyacrylamide–H_2O and polyacrylamide–H_2O–methanol gels. In H_2O gels at swelling equilibrium (good solvent conditions), the concentration dependence of the longitudinal modulus $(K + 4/3\mu)_{\text{lattice}}$ is found to vary as $c^{2.35 \pm 0.06}$. The modulus of gels formed in H_2O–methanol (poor solvent conditions) varies as $c^{3.07 \pm 0.07}$. Ancillary mechanical measurements of μ for polyacrylamide–H_2O gels (ref 20) agree remarkably well with the results of this study (see Table II).

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(22) The variance has been determined from estimates of pipetting errors, limitations of instrumental resolution, and uncertainty in fitting of data points. Note that our former suggestion, that $\alpha \simeq 4$, is in error because of an earlier misconception[1] concerning the identity of ρ.

Effects of a Nematic-Like Interaction in Rubber Elasticity Theory

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ABSTRACT: A modified theory of rubber elasticity is proposed which includes anisotropic intermolecular interactions favoring the alignment of neighboring chain segments. These interactions are described in the mean field approximation by an intermolecular potential having the same form as that used for the study of nematic phases. It is shown that such interactions increase orientation of chain segments but do not significantly alter the stress–strain behavior of a network. Finally, experimental consequences of the theory are discussed.

In recent years, the local structure of amorphous polymers has been a subject of considerable interest. In the rubbery state, the stress-induced orientation distribution of chain segments should be very sensitive to the presence of local order. The second moment S of this distribution has been calculated by Roe and Krigbaum[1] in the framework of the classical gas-like theory[2,3] of rubber elasticity. Observation of deviations from this theory is a way to approach the problem of local order in rubbers. A few data are already available in this respect. Fukuda, Wilkes, and Stein[4] reported values of the stress-optical coefficient which are too high in dry rubbers and which are reduced upon swelling. They suggested that this inconsistency could be due to some local order. Besides, the fluoresence polarization technique[5–6] has been recently extended to the study of rubbers and preliminary results[7] also show that S is anomalously higher in dry networks than in swollen ones.

This emphasized the need for a modified theory of rubber elasticity including intermolecular interactions which could give rise to anisotropic packing of chain segments. Di Marzio[8] and Jackson[9] et al. developed lattice models with anisotropic interactions which enhance the alignment of neighboring segments. Their aim was not to study orientational properties of networks but rather to account for the additional C_2 term of the phenomenological Mooney–Rivlin equation:

$$\sigma = (C_1 + C_2/\lambda)(\lambda^2 - \lambda^{-1})$$

where σ is the true stress and λ the extension ratio. Both models lead to a ratio C_2/C_1, proportional to $1/N$ (N being the number of segments per chain), which is much smaller than experimental values ($C_2/C_1 \simeq 1$). The Di Marzio theory was improved by Tanaka and Allen[10] who showed that his C_2 term should be doubled. Recently, de Gennes[11] discussed the behavior of polymeric networks containing nematogenic segments near the isotropic–nematic transition.

In the present work, the chain segments of usual rubbers are considered as cylindrically symmetric objects submitted to a weak nematic-like interaction. Segment–segment interactions are described in terms of a thermodynamic potential of the same form as that introduced in the study of nematic phases.[12,13] The stress–strain and orientation–strain relations are derived for uniaxial stretching. It is concluded that such interactions principally increase the orientation and that the mechanical behavior is not significantly altered, according to the results of Di Marzio, Jackson, and Tanaka and Allen. Finally, experimental procedures are discussed which should allow one to distinguish between nematic-like interaction and entanglement effects.

General Considerations

In a uniaxial medium, the intermolecular potential U_{12}[13] between two molecules or chain segments, which behave as cylindrically symmetric objects, depends on the intermolecular distance r_{12} and on the angles Θ_1 and Θ_2 between the molecular axes and the symmetry axis of the medium.

It can be expanded in the form:

$$U_{12} = \sum_{l\,\mathrm{even}} u_l(r_{12})P_l(\Theta_1)P_l(\Theta_2) \qquad (1)$$

where $P_l(\Theta)$ are Legendre polynomials.

Restricting the development to the first anisotropic term ($l = 2$), one obtains a contribution F_{int} to the free energy per molecule:

$$F_{\mathrm{int}} = -\tfrac{1}{2}U\langle \mathrm{P}_2(\Theta)\rangle^2 = -\tfrac{1}{2}US^2 \qquad (2)$$

where S is the second moment of the molecular distribution function and U is a positive parameter of interaction.

As a preliminary step, let us consider a chain of N segments interacting with a uniaxial medium of axis Z, the end-to-end vector $\mathbf{R}$ lying in the Z direction (Figure 1).

The free energy per segment can be expanded in the form:

$$F = aS^2 + bS^3 + \ldots + cr^2 + dr^4 + \ldots + er^2S + fr^2S^2 + gr^4S + \ldots \qquad (3)$$

where S is the second moment of the surrounding medium and $r^2 = R^2/NR_0^2$, R_0^2 referring to the free chain. The first set of terms characterizes the nematic-like interaction[14] and the second one describes the usual entropic elasticity.[2] cr^2 is the dominant Gaussian term $c = {}^3/_2kT$ and dr^4 is the first non-Gaussian term corresponding to a possible increase in the tension when the chain approaches its limit of extension. The remaining coupling terms arise from the alteration of chain elasticity due to intermolecular in-

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