for which T_g data is well fit by the form of eq 15. For PPO blended with PS oligomers, the pure-component glass-transition temperatures differ by >200 K, and the value $K_1 = 2.50$ reproduces blend transition temperatures to within 5 K.[18] Equations 16 and 17 give, respectively, $K_1 = 2.79$ and $K_1 = 1.60$. Thus, although strictly the difference between pure-component glass-transition temperatures might seem rather large for the single-term expansions necessary for eq 16 and 17, the former is the more acceptable for compatible blends of PPO and PS (for which $\Delta C_{p_2}/\Delta C_{p_1} < 1$) and, indeed, is fairly accurate.

Final Remarks

A phenomenological theory for the compositional variation of glass-transition temperatures in one-phase mixtures based on a model of these as regular solutions has now been shown to account with some success for the phenomenon in binary mixtures of high polymers and, also, to give an acceptable description of the variation of glass-transition temperatures with molecular mass for homopolymers. Further, as described in the present contribution, these two formal treatments can be combined to predict glass-transition temperatures in compatible blends of arbitrary composition and pure-component degree of polymerization from component chain end and high-polymer glass-transition temperatures and their reciprocal heat-capacity increments, equivalent to the generation of a $2n$-dimensional surface.

Acknowledgment. This research was supported by the National Science Foundation Division of Materials Research under Grant DMR79-151715, Polymers Program.

References and Notes

(1) Gordon, M.; Taylor, J. S. *J. Appl. Chem.* **1952**, *2*, 493.
(2) Wood, L. A. *J. Polym. Sci.* **1958**, *28*, 319.
(3) Kelley, F. N.; Bueche, F. *J. Polym. Sci.* **1961**, *50*, 549.
(4) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.
(5) Mandelkern, L.; Martin, G. M.; Quinn, F. A. *J. Res. Natl. Bur. Stand. (U.S.)* **1957**, *58*, 137.
(6) Gibbs, J. H.; DiMarzio, E. A. *J. Chem. Phys.* **1958**, *28*, 807.
(7) Pochan, J. M.; Beatty, C. L.; Pochan, D. F. *Polymer* **1979**, *20*, 879.
(8) Kovacs, A. J. *Adv. Polym. Sci.* **1963**, *3*, 394.
(9) Couchman, P. R.; Karasz, F. E. *Macromolecules* **1978**, *11*, 117.
(10) Couchman, P. R. *Macromolecules* **1978**, *11*, 1156; *Phys. Lett.* **1979**, *70A*, 155.
(11) Couchman, P. R. *J. Appl. Phys.* **1979**, *50*, 6043.
(12) Couchman, P. R. *J. Mater. Sci.* **1980**, *15*, 1680.
(13) Kanig, G. *Kolloid Z. Z. Polym.* **1963**, *190*, 1.
(14) Fox, T. G.; Flory, P. J. *J. Polym. Sci.* **1954**, *4*, 315.
(15) Boyer, R. F. *J. Macromol. Sci., Phys.* **1973**, *7*, 487.
(16) See, for example: Naito, G.; Johnson, G. E.; Allara, D. L.; Kwei, T. K. *Macromolecules* **1978**, *11*, 1260.
(17) MacKnight, W. J.; Karasz, F. E.; Fried, J. R. In "Polymer Blends"; Newman, S., Paul, D. R., Eds.; Academic Press: New York, 1978; Vol. II, Chapter 5.
(18) Kwei, T. K.; Frisch, H. L. *Macromolecules* **1979**, *11*, 1267.
(19) Fried, J. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1978**, *11*, 150.
(20) Ueberreiter, K.; Otto-Laupenmühlen, E. *Z. Naturforsch., A* **1953**, *8*, 664.

The Poisson Ratio in Polymer Gels

E. Geissler*

Laboratoire de Spectroscopie Optique, Université de Savoie, 73011 Chambery Cedex, France

A. M. Hecht

Laboratoire de Spectrométrie Physique,[†] Université Scientifique et Médicale de Grenoble, 38041 Grenoble Cedex, France. Received February 6, 1980

ABSTRACT: A comparison is made between the longitudinal elastic modulus and the shear modulus in polyacrylamide gels. The former is measured by inelastic light scattering as well as by osmotic deswelling; the latter is measured by observation of the frequency of standing waves excited in the samples. The ratio of these two quantities is found, within experimental error, to be equal to 2 in a poor solvent (1:3 methanol–water at 11.5 °C), as is to be expected from the Gaussian nature of the polymer chains in Θ conditions (the Poisson ratio σ of the polymer coils is equal to zero). In a good solvent, a scaling argument based on the Flory expression for the free energy predicts that $\sigma = {}^1/_4$. The experimentally measured values are significantly larger and increase as the quality of the solvent improves.

I. Introduction

When solvent is removed from a polymer solution or a gel, there is an accompanying increase in the osmotic pressure, the magnitude of which defines the osmotic elastic modulus of the medium. In the semidilute region the elastic modulus follows a scaling law as a function of polymer concentration c: it is proportional to c^a, where the exponent a is 2.25 in a good solvent[1] and equal to 3 in a Θ solvent.[2] These theoretical predictions have been confirmed by neutron scattering measurements of the coherence length in polymer solutions,[3,4] by direct mechanical measurements on gels in a good solvent,[5,6] and by inelastic light scattering for gels in a poor solvent.[7]

In each of the above theoretical and experimental investigations it is assumed that there is no behavioral distinction between the osmotic bulk modulus K and the shear modulus μ (or any combination of the two, such as the longitudinal elastic modulus $E = K + 4\mu/3$). Although it might seem surprising that μ, which describes a deformation unaccompanied by a change in solvent concentration, should be related to the osmotic pressure, this must nonetheless be so: both K and μ are related in the same way to the tension acting on the polymer chains and the number of tie points in the network. Candau et al.[8] have recently been able to demonstrate this property by showing that the variation of E deduced from light scattering measurements on polystyrene–benzene gels (good-solvent conditions) follows closely variations in μ.

In contrast with the above results, the present authors have previously found that in the system polyacrylamide–water E and μ, measured, respectively, by light scattering and mechanical methods, apparently enjoy different types of behavior with concentration. It was

[†] CNRS Associate Laboratory.

0024-9297/80/2213-1276$01.00/0

found that at room temperature E is proportional to $c^{2.35\pm0.06}$, while the exponent for μ is noticeably larger.[9] Recently, Gelman and Nossal[10] obtained an exponent for μ in this system whose value is close to 3. In an attempt to understand this discrepancy, which appears to be real, we decided to investigate the ratio E/μ in a series of polyacrylamide gels under different conditions of solvent. Because of the relations which hold between the various elastic moduli, this is tantamount to a measurement of the microscopic Poisson ratio σ (not to be confused with the short-time macroscopic Poisson ratio, the value of which is approximately $^1/_2$, in which the solvent does not have time to escape from the polymer matrix).

In the following section an account is presented of the behavior expected for the Poisson ratio on deswelling for two cases of interest, namely, Θ- and good-solvent conditions. In the third section the experimental arrangements are described, and in the last are contained the results and discussion.

II. Theory

As indicated in the previous section, for the longitudinal elastic modulus E one is interested in a *relative* motion between the polymer and the solvent: as the gel under consideration is squeezed by a uniaxial stress, the solvent contained in the matrix is forced out. As this process is extremely slow for samples of macroscopic size due to the large frictional forces involved, it is convenient to visualize the process occurring in a single monomer coil. The dimensions of the coil are taken as $R_\parallel$ parallel to the applied stress and $R_\perp$ perpendicular to the applied stress.

Θ Solvent. In Θ conditions the equilibrium radius of the coil in the absence of stress is

$$R_\parallel = R_\perp \sim N^{1/2}b \tag{1}$$

where N is the degree of polymerization and b is the length of the independent chain unit. The chain obeys Gaussian statistics, so that the projections of the coil along three orthogonal directions are independent. In other words, when the chain is compressed along the parallel axis, $R_\perp$ is unaltered. The Poisson ratio is therefore

$$\sigma = -\mathrm{d}R_\perp/\mathrm{d}R_\parallel = 0 \tag{2}$$

This assumption was made explicitly by Tanaka et al.[11] for polyacrylamide gels.

Good Solvent. In a good solvent the presence of the excluded volume couples the three radii of gyration with each other. To calculate σ, we recall the Flory formalism for the free energy of the polymer coil.

In a good solvent in three dimensions an unhindered polymer coil expands from its radius of gyration in Θ conditions R_0 to a larger value R. At temperature T and polymer concentration $c = N/R^3$, the Flory free energy of the coil can be expressed in terms of the excluded volume[12] v

$$F = TR^2/R_0^2 + vTc^2R^3 \tag{3}$$

where constant proportionality factors have been omitted.

Now the mean radius of gyration is given by

$$3R^2 = R_\parallel^2 + 2R_\perp^2 \tag{4}$$

and the volume of the coil is

$$R^3 = R_\perp^2 R_\parallel \tag{5}$$

where $R_\perp$ and $R_\parallel$ have the same meaning as above and $R_\parallel$ is imposed by the external constraint on the coil. Expression 3 must therefore be minimized with respect to $R_\perp$, giving

$$R_\perp^4 R_\parallel = 3N^3vb^2/2 \tag{6}$$

It follows therefore that the Poisson ratio

$$\begin{aligned}\sigma &= -\partial R_\perp/\partial R_\parallel \\ &= R_\perp/4R_\parallel \\ &= 1/4\end{aligned} \tag{7}$$

for small deformations of the coil.

It should be pointed out that eq 6 is not a new result. It was obtained by Daoud and de Gennes,[13] who used a scaling argument to investigate the behavior of a polymer coil in a good solvent forced into a narrow slit of width $R_\parallel$. Their result can be expressed in the form

$$R_\perp = R_F^{5/4}R_\parallel^{-1/4} \tag{8}$$

which is identical with eq 6 and hence leads to the same conclusion that $\sigma = {}^1/_4$. R_F in eq 8 refers to the unperturbed Flory radius in three dimensions.

On substituting the value $\sigma = {}^1/_4$ into the relation[17]

$$E/\mu = 2(1-\sigma)/(1-2\sigma) \tag{9}$$

one obtains E/μ equal to 3. In the polymer phase diagram of Daoud and Jannink,[2] in semidilute solutions the good-solvent region occurs at low polymer concentrations; increasing the concentration at the same temperature shifts the solution into the poor-solvent region. It follows that the transition from the good-solvent condition, where $\mu = E/3$, to the poor-solvent condition, where $\mu = E/2$, must cross an intermediate region (the "crossover" region) in which μ will have a steeper slope than E as a function of concentration.

In the next section are described the experimental techniques used to measure E and μ.

III. Experimental Techniques

For the sequence of poor-solvent gels, polyacrylamide in a solvent containing 75% water with 25% methanol (by volume) was used. The samples were prepared as described in ref 7, and the experiments were conducted at 11.5 °C. This temperature has previously been found to be the Θ temperature for the equivalent polymer solution.[7]

To obtain good-solvent conditions, on the other hand, the polyacrylamide–water system was used. Although the Θ temperature for this system is not known with precision, it can be concluded from the observations of Tanaka et al.,[14] who detected a spinodal point at −17 °C in a 2.5% sample, that the Θ temperature is in the neighborhood of −20 °C. Thus a 3% sample at 27 °C should lie well within the good-solvent region defined by Daoud and Jannink: if c is the polymer concentration and τ the reduced temperature (with respect to the Θ temperature), then c/τ is about 0.16 and is comfortably smaller than the crossover value of unity. However, at concentrations close to 3% a catastrophic drop in shear modulus has been observed, which was attributed to the increasing proportion of pendent chains.[9] Although this interpretation is possibly incorrect, this complication was avoided by using samples of 6% and the experiments were carried out at 27 °C as well as 73 °C (c/τ values approximately 0.32 and 0.16, respectively). It should be mentioned in support of these approximate figures that the measurements of E reported in ref 9 indicate that the good-solvent region extends, at 21 °C, to 17% in concentration ($c/\tau \sim 1.05$).

The sample preparation for the good-solvent gels was carried out as described in ref 9. The ratio of acrylamide to bisacrylamide used in these samples was 37.5:1.

Shear Modulus. Two methods were used to determine the shear moduli of the gels: observation of the deformation induced in a sample of known cross section under a given strain[9] and detection of the normal modes of vibration in the sample enclosed in an optical cell.[10,15] The first was used only for measurements at room temperature, while the second was used at all other temperatures. The measurements described here were based on the observation of the fundamental vibrational mode[10] excited in a gel housed in a rectangular glass optical cell of dimensions $a \times b \times c$. An external stimulus, provided by contact of the sample

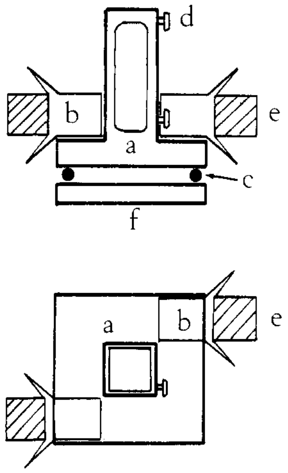

Figure 1. Experimental arrangement used for the observation of standing waves in the gels: (a) copper sheath with heavy base for holding the glass sample cell; (b) miniature loudspeakers attached to the base of the sample holder; (c) ball-bearing mounting allowing free rotation about the vertical axis; (d) retaining screws to fix the cell in the holder; (e) rigid lucite rod connecting the loudspeaker diaphragm to the fixed outer thermal shield (not shown) (the loudspeaker membranes are thus stationary, the movement being imparted to the heavy casing and the sample holder); (f) thermoelectric temperature regulator.

holder with a miniature loudspeaker, excites the gel. Irradiation by a low-power laser beam permits the response of the gel to be detected by a photomultiplier, the output current of which is analyzed by an autocorrelator. The observed frequencies were found to be reproducible to within the precision of the 128-channel correlator. A step-function waveform, generated by a manual reversing switch and 4.5-V battery, was used as the exciting signal to the loudspeakers. Acceptable autocorrelation functions could be generated after ten or so switch reversals, separated by intervals of 1 or 2 s.

To identify the fundamental frequency it is essential to define accurately the prevailing boundary conditions. To this end the sample cell was locked tightly into a loosely mounted heavy copper holder, weighing about 30 times more than the sample; this copper holder, which was also the thermal sheath for the temperature regulation, was the coupling element between the loudspeakers and a rigid support (see Figure 1). The second consideration is that for small stresses polyacrylamide gels adhere to the walls of the glass cells.[16] These two conditions guarantee that the displacement u of the gel at the boundary of the cell is vanishingly small.

The equation of motion of the gel in the cell is[17]

$$\frac{\partial^2 \mathbf{u}}{\partial t^2} = c_t^2\nabla^2\mathbf{u} + (c_l^2 - 2c_t^2)\nabla\nabla\cdot\mathbf{u} \qquad (10)$$

where the damping terms have been neglected and c_t and c_l are, respectively, the transverse and longitudinal velocities. Equation 10 has been solved by Nossal[15] for gels in a rectangular cell with two sets of boundary conditions: freely slipping surfaces and surfaces which can move freely perpendicular to the cell walls. For polyacrylamide gels formed in the cuvette, the boundary conditions are probably given by $\mathbf{u} = 0$ at the glass walls: although the solutions for this case are not simple, it has been observed[10] that there is good agreement between the values of the elastic modulus μ obtained by mechanical compression and those obtained from the relation

$$\omega = k(\mu/\rho)^{1/2} \qquad (11)$$

where ω is the angular frequency of the fundamental mode of wave vector $\mathbf{k}$.

In order to determine the wave vector of the fundamental mode, a series of five gels of differing composition and solvent (water and methanol–water) were measured by the light scattering technique at room temperature and then extracted from their glass cell for the shear modulus to be measured by deformation under uniaxial strain. It was found that

$$k_{\min} = (2.24 \pm 0.13)\pi/a \qquad (12)$$

In all cases the depth of the gel was close to 3 cm, with $a = 1$ cm.

Longitudinal Elastic Modulus. The present authors have made measurements of E in polyacrylamide gels by inelastic light scattering.[7,9] Since the values deduced are the product of several factors each of which is imprecisely known, it is reasonable to object to their use here in the absence of independent confirmation.

Recently, a new method has been developed to measure E by osmotic deswelling of gels in a good solvent.[18] Briefly the method is as follows. A sample of gel at uniform concentration c_∞ is pushed into contact with a semipermeable membrane (a large-pore Millipore filter is used) under a hydrostatic pressure P. At the instant of contact, that part of the sample touching the filter immediately adjusts its concentration, by ejection of solvent through the filter, to a new value c_0, the osmotic pressure of which just compensates the applied pressure P. The resulting movement can be visualized as the collapse of the gel to form a porous plug of concentration c_0 and of thickness q. If the rate of advance of the low-concentration end of the gel is denoted by v, then the thickness of the plug is the time integral of the rate of accretion of polymer onto the plug

$$q = \frac{c_\infty}{c_0 - c_\infty}\int v\,\mathrm{d}t \qquad (13)$$

The volume flow of the solvent through the plug is given by the pressure gradient divided by the friction coefficient f, P/qf, diminished by a counterflow due to the collective diffusion coefficient[11] D_c $(=E/f)$ in the collapsing gel. Clearly, the restoring elastic modulus E is that of the gel at concentration c_∞ as it impinges on the plug, while the friction coefficient limiting the counterflow is that of the plug. Hence

$$v = (P - E)/qf \qquad (14)$$

Algebraic manipulation of eq 13 and 14 leads to the following expression for v:

$$v = [(P - E)(c_0 - c_\infty)/2c_\infty ft]^{1/2} \qquad (15)$$

Two limiting cases of the above expression are of interest. The first is where there is a strong affinity between the polymer of the gel and the material of the membrane. The concentration c_0 is then much larger than c_∞ and independent of the applied pressure. This is the case for polyacrylamide–water in contact with the Millipore filters used (identical results are obtained with ordinary large-pore laboratory filter paper). The friction coefficient is proportional to c_0, and v^2 is observed to be inversely proportional to the elapsed time and the applied pressure P. The agreement found between the value of E obtained by light scattering and those obtained in this fashion[18] is very satisfactory. This technique was used to measure E for the polyacrylamide–water samples described here.

The second case of interest is where the polymer interacts weakly with the filter material, and therefore c_0 is a function of the applied pressure. This is the case for polyacrylamide–methanol–water. Although v is still inversely proportional to $t^{1/2}$, the pressure dependence of the deswelling process now depends on the relation between the osmotic pressure and the gel concentration and is complicated in this instance by the binary nature of the solvent. These considerations make it difficult to extract an unambiguous value of E from the deswelling measurements for the case of the poor solvent.

The agreement obtained between the two techniques for the good-solvent condition, however, lends support to the validity of the light scattering method in general and is thus an encouragement to its use in the case of poor solvent. The light scattering measurements for the poor-solvent regime have already been reported[7] and so were not repeated here. The samples for the shear modulus measurements, however, were prepared in exactly the same way as in ref 7. The ratio of acrylamide to bisacrylamide used was 75:1.

IV. Results and Discussion

Poor Solvent. Figure 2 shows on a double-logarithmic plot the results of the shear modulus measurements ob-

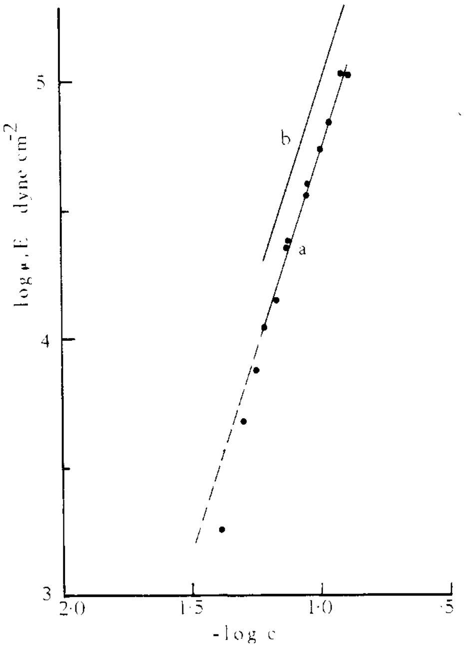

Figure 2. Values of shear elastic modulus μ of polyacrylamide–methanol–water gels at 11.5 °C as a function of polymer concentration on a log–log plot. The least-squares straight line a is obtained from those points with concentration ranging between $c = 0.06$ and $c = 0.13$ g cm^{-3} and is given by $\log \mu = 7.843 + 3.116 \log c$. The straight line denoted b is obtained by inelastic light scattering from ref 7 and represents the variation of the longitudinal elastic modulus E at the same temperature and over the same concentration range. The equation describing b is $\log E = 8.090 + 3.102 \log c$. The fact that for concentrations less than 6% the experimental values of μ fall below the extrapolated scaling relation suggests that pendent chains are present.

tained from the polyacrylamide–methanol–water samples at 11.5 °C using relation 11. In the region between $c = 0.06$ and $c = 0.13$ g cm^{-3} (i.e., the same region as investigated by light scattering) a linear relation holds, described by

$$\mu = 6.97 \times 10^7 c^{3.12} \text{ dyn cm}^{-2} \qquad (16)$$

The equivalent relation for the longitudinal elastic modulus was found to be[7]

$$E = 1.148 \times 10^8 c^{3.07} \text{ dyn cm}^{-2} \qquad (17)$$

The exponents in these two equations are the same within experimental error (±0.07), thus confirming that in a poor solvent E and μ display the same behavior. The ratio E/μ for $c = 0.1$ is

$$E/\mu = 1.85 \qquad (18)$$

This ratio is to be compared with the theoretically expected value of 2 (corresponding to $\sigma = 0$). It should be mentioned that there are two extra contributions to the scattered light, both of which tend to lower the apparent value of E: multiple scattering, which is difficult to eliminate near the Θ temperature, and an extra component due to the ternary nature of the scattered light. These contributions, which were estimated each to be less than 10% of the total intensity, were not known with precision, and were neglected in the calculation of E. Correction for these effects would enhance the value of E in the same proportions and thereby improve the agreement between the theoretical and experimental values of E/μ. The intrinsic error in the light scattering method is, however, of the order of 10%, and it must therefore be concluded from the values of E and μ found that the Poisson ratio of a gel in a poor solvent is zero, within the error of the experiment.

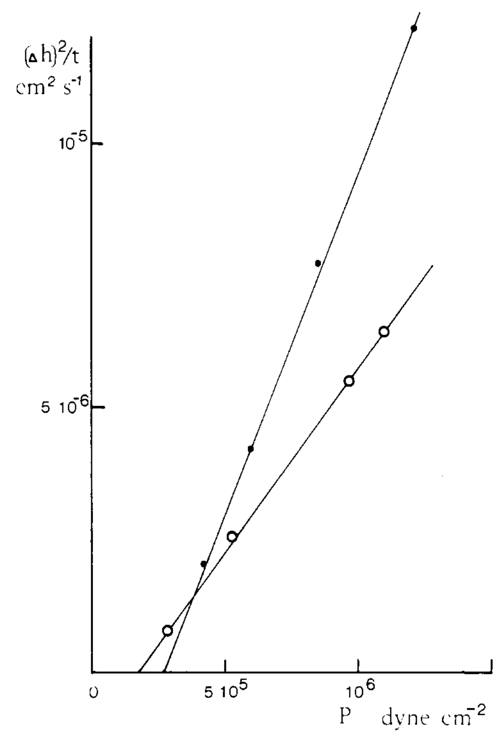

Figure 3. Measurements of $(\Delta h)^2/t$ against applied pressure under reverse osmosis for polyacrylamide–water gels of concentration $c = 0.065$ g cm^{-3}, where Δh is the change in position of the free-gel meniscus as a function of the elapsed time t: (○) $T = 27$ °C; (●) $T = 73$ °C. The intercept with the horizontal axis is equal to the longitudinal elastic modulus E.

Good Solvent. As stated in section III, samples of nominal concentration 6% were used, with pure water as the solvent, to avoid the putative effects of pendent chains which become apparent at the lower concentrations in polyacrylamide gels. The effective concentration, measured by weighing before and after baking the samples to dryness, was 0.065 g cm^{-3}. At 27 °C measurement of E yielded (see Figure 3)

$$E_{27\,°\mathrm{C}} = (1.70 \pm 0.14) \times 10^5 \text{ dyn cm}^{-2} \qquad (19)$$

(This should be compared with 1.76 × 10^5 dyn cm^{-2} by light scattering.) The corresponding result, also obtained by osmotic deswelling, for 73 °C is

$$E_{73\,°\mathrm{C}} = (2.69 \pm 0.09) \times 10^5 \text{ dyn cm}^{-2} \qquad (20)$$

The quoted errors are the standard deviations in the slopes arising from the dispersion in the experimental points.

For the shear moduli at these two temperatures, several samples were made of the same nominal concentration. Although the measurement of μ for each sample was reproducible to within the precision of the frequency measurement (<2%), variations were observed from sample to sample, probably caused by slightly varying conditions of polymerization, such as temperature, dissolved-oxygen content, etc. The mean values are

$$\mu_{27\,°\mathrm{C}} = (4.54 \pm 0.20) \times 10^4 \text{ dyn cm}^{-2}$$
$$\mu_{73\,°\mathrm{C}} = (5.28 \pm 0.14) \times 10^4 \text{ dyn cm}^{-2} \qquad (21)$$

Combining these results, one finds

$$E_{27\,°\mathrm{C}}/\mu_{27\,°\mathrm{C}} = 3.74 \pm 0.35$$
$$E_{73\,°\mathrm{C}}/\mu_{73\,°\mathrm{C}} = 5.09 \pm 0.22 \qquad (22)$$

Both of these results are significantly larger than the value 3 expected from scaling considerations, and the discrepancy increases as the solvent improves ($c/\tau \rightarrow 0$).

In terms of the Poisson ratio the results quoted in eq 22 can be expressed as

$$\sigma_{27\,^\circ\mathrm{C}} = 0.318 \pm 0.023$$
$$\sigma_{73\,^\circ\mathrm{C}} = 0.378 \pm 0.006 \qquad (23)$$

In conclusion, it appears that in Θ conditions the Poisson ratio σ of a polymer gel is equal to zero within experimental error. This is the behavior to be expected from polymer coils obeying Gaussian statistics.

In a good solvent, on the other hand, the experimental results presented here suggest that the polymer coil is less compressible than is implied by the Flory expression for the free energy. It should, however, be emphasized that the measurements were made on unswollen gels; that is, although their thermodynamic state is well defined (as witnessed by the scaling-law variation of E with polymer concentration[9]), there is overlap between adjacent polymer coils. However, in the absence of measurements on swollen gels, such an explanation for the observed discrepancy remains speculative for the moment.

Acknowledgment. We thank Y. Ayant for helpful conversations and express our gratitude to R. Nossal for his very constructive criticisms of the original text.

References and Notes

(1) P. G. de Gennes, *Macromolecules*, **9**, 587, 594 (1976).
(2) M. Daoud and G. Jannink, *J. Phys. (Paris)*, **37**, 973 (1976); F. Brochard and P. G. de Gennes, *Macromolecules*, **10**, 1157 (1977).
(3) M. Daoud, J. P. Cotton, B. Farnoux, G. Jannink, G. Sarma, H. Benoit, R. Duplessix, C. Picot, and P. G. de Gennes, *Macromolecules*, **8**, 804 (1975).
(4) J. P. Cotton, M. Nierlich, F. Boué, M. Daoud, B. Farnoux, G. Jannink, R. Duplessix, and C. Picot, *J. Chem. Phys.*, **65**, 1101 (1976).
(5) J. P. Munch, S. Candau, J. Herz, and G. Hild, *J. Phys. (Paris)*, **38**, 971 (1977).
(6) A. Belkebir-Mrani, J. E. Herz, and P. Rempp, *Makromol. Chem.*, **178**, 485 (1977).
(7) E. Geissler and A. M. Hecht, *J. Phys. (Paris)*, **39**, 955 (1978).
(8) S. J. Candau, C. Y. Young, T. Tanaka, P. Lemaréchal, and J. Bastide, *J. Chem. Phys.*, **70**, 4694 (1979).
(9) A. M. Hecht and E. Geissler, *J. Phys. (Paris)*, **39**, 631 (1978).
(10) R. A. Gelman and R. Nossal, *Macromolecules*, **12**, 311 (1979).
(11) T. Tanaka, L. O. Hocker, and G. B. Benedek, *J. Chem. Phys.*, **59**, 5151 (1973).
(12) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1967.
(13) M. Daoud and P. G. de Gennes, *J. Phys. (Paris)*, **38**, 85 (1977).
(14) T. Tanaka, S. Ishiwata, and C. Ishimoto, *Phys. Rev. Lett.*, **38**, 771 (1977).
(15) R. Nossal, *J. Appl. Phys.*, **50**, 3105 (1979).
(16) When the temperature of the gel is lowered, there is a small degree of syneresis between the gel and the confining glass cell. The principal effect of this is to dampen the standing mode observed; the frequency, however, remains unchanged. It must be concluded that the slippage occurring at the boundary is not sufficient to change the nature of the mode.
(17) L. D. Landau and E. M. Lifshitz, "Theory of Elasticity", Pergamon Press, Oxford, 1970, Chapter 3.
(18) A. M. Hecht and E. Geissler, *Polymer*, in press.

Dynamics of Semiflexible Polymers in Solution

D. W. Schaefer*[†]

Sandia National Laboratories,[†] *Albuquerque, New Mexico 87185*

J. F. Joanny and P. Pincus

Department of Physics, University of California at Los Angeles,
Los Angeles, California 90024. *Received November 30, 1979*

ABSTRACT: The statistical properties of semiflexible polymers are analyzed throughout the temperature–concentration plane above the Θ temperature. At intermediate (semidilute) and high concentrations, polymers which are stiff on the scale of a few monomers are found to differ from completely flexible chains. For semiflexible chains, scaling methods have limited validity compared to completely flexible chains. Mean-field methods are found to be appropriate to most semiflexible systems of intermediate-solvent quality. Experimental data are presented on dilute, semidilute, and concentrated solutions of polystyrene in tetrahydrofuran, ethyl acetate, and methyl ethyl ketone, representing good and marginal solvents. The dilute-solution data are used to characterize independent chain statistics and this information is then used to generate the appropriate temperature–concentration diagram covering higher concentrations. In semidilute solution, predicted crossovers are observed in the concentration dependence of dynamical properties. At volume fractions approaching unity, however, dynamical properties become concentration independent and do not show Θ-like scaling observed in small-angle scattering and predicted by mean-field theory. This discrepancy is attributed to the limited width of the Θ-like regime and to differences in the statistical averages being probed in dynamic vs. static techniques.

I. Introduction

A considerable body of evidence indicates that the properties of chain molecules in solution do not change smoothly as a function of density ρ.[1] Rather a distinct change in behavior is observed at the monomer density ρ^* at which the domains of individual molecules overlap. For example, the radius of gyration, R_g, of a single chain is nearly independent of density for $\rho < \rho^*$ but scales as a power of ρ for $\rho > \rho^*$ ($R_g \sim \rho^{-z}$) where the scaling exponent z is 0.125 for polymers dissolved in good solvents. In this work we study the density dependence of the dynamics of semiflexible chain molecules in good and marginal solvents. In good solvents, we find behavior expected on the basis of scaling concepts, consistent with the experiment of Adam and Delsanti.[2] In the case of marginal solvents, however, we postulate a new regime in the temperature–concentration diagram where the system is more

---

[†] A U.S. Department of Energy facility.

0024-9297/80/2213-1280$01.00/0