The Poisson Ratio in Polymer Gels. 2

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ABSTRACT: We report measurements of the ratio of the longitudinal elastic modulus E to the shear modulus μ for a series of equilibrium-swollen polyacrylamide–water gels, using quasi-elastic light scattering and mechanical observations, respectively. It is found that the ratio E/μ is equal to 2 within experimental error for gels whose concentration before swelling was about 6%; this is the value of E/μ expected of a gel in a poor solvent. For samples of lower concentration, the ratio E/μ rises to 2.7 ± 0.3, closer to the theoretically expected value of 3 for gels in good solvents. Our previous measurements in unswollen gels in a good solvent gave values of the ratio lying between 4 and 5. In this investigation it is shown that E varies as $c^{2.25}$ within experimental error as the gel is swollen; μ, on the other hand, is almost independent of swelling.

In a previous paper[1] we reported measurements in polyacrylamide gel networks of the ratio of the longitudinal elastic modulus to the shear modulus. This ratio is equal, in a continuous medium, to

$$E/\mu = 2(1 - \sigma)/(1 - 2\sigma) \quad (1)$$

where σ is the Poisson ratio of the gel network. It is understood that the Poisson ratio referred to is that in which the solvent can freely leave the gel; this is of necessity different from the short-time gel Poisson ratio (in which the composition of the gel remains unchanged), the value of which is close to 0.5.

The continuous-medium approximation is justified by the large number of degrees of freedom existing in any given polymer chain making up the array. In ref 1 it was found for gels in poor-solvent conditions, where the polymer coils are Gaussian, that $\sigma = 0$ within experimental error. For polyacrylamide–water gels, on the other hand, σ was found to be close to 0.4, and its value appeared to increase for increasingly good-solvent quality.

In order to form a picture of the good-solvent region, we proposed a model for the gel consisting of an array of separate Flory coils, each acting as if it were subject only to its own excluded volume and unaffected by neighboring polymer coils. This arrangement was found to have a Poisson ratio equal to 0.25. We speculated that the origin of the discrepancy between experiment and the theoretical prediction issued from this model lay in the fact that our gels were measured in the same unswollen state as they were prepared, in which significant overlap may exist between adjacent coils.[1]

In this paper we report similar measurements on polyacrylamide–water gels swollen to equilibrium, for which the coil overlap is expected to be reduced. In the present work, the measurements of E were made by dynamic light scattering[2,3] while μ was measured by observation of the static deformation produced by a uniaxial strain.

The above picture of the gel is a slightly simplified version of that outlined by Flory,[4] in which the shear modulus of cross-linked polymers is seen as resulting from the density of elastically active coils in the network. For a given cross-linked gel, in which all the coils are elastically active (i.e., each polymer chain has both ends attached to distinct cross-linking points forming the matrix), one might expect that the number of elastic chains will not vary on swelling or deswelling of the gel. Hence the density of such elastic chains should vary as the total polymer concentration (subject to a small correction factor caused by a logarithmic term in the entropy,[4] which we neglect here). If loops or chains attached by only one end to the matrix are present, these might be expected to contribute to the elastic modulus through nonpermanent entanglements when the gel is deswollen but not to be effective at large degrees of swelling. The variation of μ with swelling is therefore expected to be proportional to the concentration c in the disentangled region and to some higher power of c, depending on the distribution of loops and one-ended chains, in the region where entanglements come into play.

In the next section we describe the experimental procedure; in the last part we discuss the discrepancies between the observations and the above picture of a gel.

Experimental Procedure

Samples of polyacrylamide were prepared as described in ref 3, using the same batch of acrylamide (A) and bisacrylamide (B) from Merck. Two concentrations were prepared, 0.033 and 0.065 g cm^{-3}, each with two A/B ratios, 37.5 and 75. Details of the samples are given in Table I. The samples were made in cylindrical containers in such a way that their initial dimensions were well-defined. After removal from the mold, they were placed at room temperature under a light, freely sliding piston, the displacement of which was measured as a function of the load added. This enabled the shear modulus to be calculated. The samples were then placed in a bath of distilled water, to which had been added 100 ppm of sodium azide to prevent bacterial growth, and left in a closed vessel for periods between 1 and 4 months for swelling equilibrium to become established. At the end of this period the samples were removed from the bath and their linear dimensions and weight were measured to determine the swelling ratios. The measurements of μ were then repeated. Segments of the samples were then cut out with a razor blade and placed in rectangular glass optical cells with additional water, and the intensity of the dynamically scattered light[2,3] was measured, using as a standard a sample of polystyrene in cyclohexane at 45 °C. The samples were subsequently weighed, then evaporated to dryness, and weighed again, thus giving the polymer concentration in the swollen gel. The longitudinal elastic modulus E of the swollen gels can then be calculated and is included in Table I.

Our past experience of making polyacrylamide gels suggests that the errors in our preparation technique give a scatter of about 2% in the total polymer concentration with respect to the target concentration. Table I indicates that the final gel concentrations calculated from the observed swelling ratio and the final concentration after swelling are systematically lower than the target concentrations. The discrepancy is larger than our estimated error in preparation and can be attributed to the elution of the sol fraction during the swelling process. From these data, for the gels initially at 6%, the average gel fraction is calculated to be

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Table I
Details of the Polyacrylamide–Water Samples Used in These Experiments

sample	A/B[a]	target concn, g cm^{-1}	final concn, g cm^{-1}	swelling ratio[b]	μ_{init}, dyn cm^{-2}	μ_{final}, dyn cm^{-2}	E_{final}, dyn cm^{-2}	$D_{c\,final}$, cm^2 s^{-1}	T, K	E_{final}/μ_{final}
1	75	0.033	0.0104	2.55	1.40×10^3	1.03×10^3	2.75×10^3	1.39×10^{-7}	292.8	2.66
2	37.5	0.033	0.0144	1.90	3.00×10^3	2.29×10^3	5.61×10^3	2.15×10^{-7}	291.3	2.44
3	37.5	0.033	0.0160	1.85	2.83×10^3	2.49×10^3	7.42×10^3	2.18×10^{-7}	292.2	2.98
4	75	0.065	0.0271	2.06		1.31×10^4	2.51×10^4	3.74×10^{-7}	292.7	1.91
5	75	0.065	0.0328	1.77	2.55×10^4	1.99×10^4	3.76×10^4	4.06×10^{-7}	292.5	1.88
6	75	0.065	0.0343	1.82	1.65×10^4	1.55×10^4	3.51×10^4	3.90×10^{-7}	291.6	2.25
7	37.5	0.065	0.0439	1.41	3.27×10^4	3.08×10^4	6.04×10^4	4.35×10^{-7}	290.3	1.94
8	37.5	0.065	0.0469	1.36	3.63×10^4	3.36×10^4	6.82×10^4	4.44×10^{-7}	289.9	2.01
9	37.5	0.065	0.0481	1.40		3.86×10^4	8.85×10^4	5.23×10^{-7}	293.0	2.26

[a] Weight ratio of acrylamide to bisacrylamide in the sample precursor fluid. [b] Ratio of final to initial sample weights.

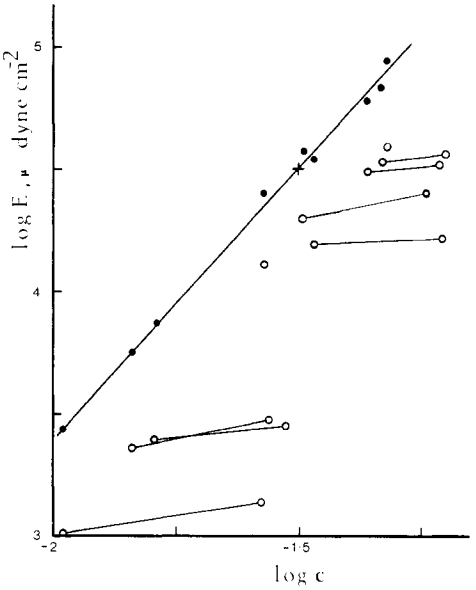

Figure 1. Measurements of E and μ as a function of gel concentration at swelling equilibrium: (●) E; (○) μ. The values of μ in the unswollen gels are shown at the high-concentration end of the connecting lines, the swelling equilibrium values at the low-concentration end. The two unpaired points were measured only at swelling equilibrium. The average value of the slopes of the connecting lines is 0.28 ± 0.13. The point denoted + is the value of E obtained from the measurements on unswollen polyacrylamide–water gels[3] extrapolated to log c = −1.5.

94 ± 6%, while that of the initially 3% gels is 84 ± 4%.

Both the shear modulus and the equilibrium swelling ratio of these gels are very sensitive to the number of defects in the network. The disparities apparent in Table I between samples of nominally identical composition are probably a consequence of different ambient temperature and dissolved-oxygen concentration in the water used at the moment of preparation. The samples were made at different times over a 3-month period.

The errors associated with the measurements of both the longitudinal and the shear elastic moduli are about 10%.

Although it is not directly germane to the purpose of this paper, the collective diffusion coefficient D_c obtained from the light scattering measurements has been included in Table I. The process of swelling reduces the gel concentrations to values well below those reported in our earlier measurements,[3] where it was found that D_c varied approximately as $c^{0.65}$. The theoretically expected value[5] for low concentrations is $c^{0.75}$. Other investigators[6] have also reported exponents smaller than 0.75. The average slope obtained from the data of Table I is

$$D_c \propto c^{0.77\pm0.06} \tag{2}$$

Although the error bar is somewhat large, it appears that the concentrations attained here are sufficiently low for the straightforward predictions concerning the hydrodynamic screening length to apply.

Results and Discussion

In Figure 1 are displayed the elastic moduli data of Table I, plotted in a double-logarithmic representation. For the shear modulus μ, apart from two samples for which the initial value of μ was not measured, each sample is represented by two open circles corresponding to the initial and final concentrations. As a guide for the eye, the two points for each sample are joined by a straight line. If the comments in the first section on the swelling dependence of μ were valid, the slope of these connecting lines would be at least unity, since the density of elastic chains decreases as the gel swells; in fact, the average slope of the connecting lines in Figure 1 is 0.28 ± 0.13. The reason for this apparent insensitivity of μ to swelling is not known.

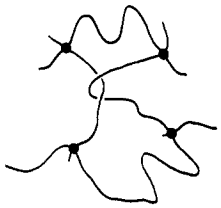

Figure 2. Schematic representation of a structural entanglement. The filled circles represent cross-linking points. At high degrees of swelling of the gel, the entanglement may act much like a cross-link. The presence of such configurations might compensate partially for the rarefaction of cross-links as the gel swells.

A possible cause may be looked for in structural entanglements built into the gel, such as that sketched in Figure 2: at low degrees of swelling, such an entanglement would not appreciably decrease the entropy of either entangled chain; however, in a highly swollen gel this entanglement will act much like a cross-link. If these internal constraints are indeed the cause of the observed relative invariance of μ with swelling, it follows that the density of such structural entanglements must be comparable to that of the cross-linking points.

Turning our attention to the longitudinal modulus E, we see in Figure 1 that the experimental points fit the straight line

$$\log E = 7.773 + (2.18 \pm 0.06) \log c \qquad (3)$$

In comparison, our previous light scattering measurements on the unswollen gels in a higher concentration range gave[3]

$$\log E = 8.027 + (2.35 \pm 0.06) \log c \qquad (4)$$

The extrapolation of eq 4 to the point $\log c = -1.5$ is shown as a cross in Figure 1. In view of the fact that the heterodyne light scattering intensity measurements are subject to errors of at least 10%, the consistency between the two independent sets of measurements 3 and 4, and their concordance with the theoretically expected slope of 2.25, is noteworthy. It should be emphasized that the errors quoted for the slopes in eq 3 and 4 are merely those due to the scatter in the experimental points; the true probable error will almost certainly be larger.

From the results described by eq 3 and 4, we conclude that the longitudinal elastic modulus E of a gel in a given solvent and at a given temperature is confined to a line defined by the gel concentration alone, which is independent of the method of preparation or the degree of swelling with respect to some reference state. It seems likely that this property pertains to the osmotic part of E, namely, κ, the bulk modulus of the network. The shear contribution of E, $4\mu/3$, according to what has been stated above, is strongly dependent on the conditions of preparation.

Evidence in favor of the above conclusion is found in observations of osmotic deswelling of these gels. By placing a gel in contact with a mobile piston through which the solvent can escape via a filter membrane, we were able to obtain the concentration of the gel for any equilibrium position of the piston, simply by measuring the position of the piston (Figure 3). The osmotic pressure of the gel is measured as a function of concentration by applying various loads to the piston. Figure 4 shows the results of these measurements performed at room temperature on an initially 0.033 g cm^{-3} polyacrylamide–water gel. The slope of the line through the experimental points is 2.26 ± 0.15. Moreover, the value of $E = c(\partial\pi/\partial c)$, measured by an osmotic deswelling technique,[7] lies above the straight-line fit to the osmotic pressure results, separated by a factor of 2.27 ± 0.14. Both these results indicate once again that the longitudinal elasticity of the gels depends only on the concentration and not on the way in which a given concentration is reached.

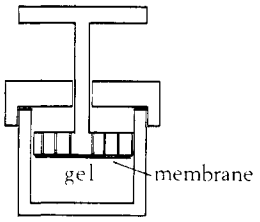

Figure 3. Apparatus used for measuring the osmotic pressure of the gel. The sliding piston contains a Millipore filter support and an array of holes to permit the solvent to pass into the upper part of the chamber. The piston is separated from the gel by a Millipore MF grade filter. The concentration of the gel is measured by observing the height of the piston above the base of the gel. The apparatus, which is constructed of lucite, is transparent.

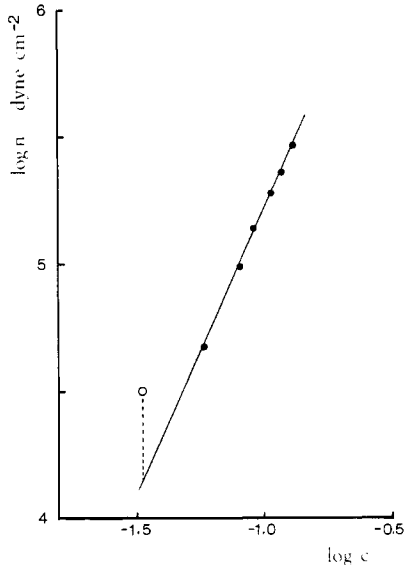

Figure 4. Osmotic pressure π of a polyacrylamide–water sample of initial concentration 0.033 g cm^{-3}. The slope of the straight line is 2.26 ± 0.15. The point indicated by an open circle is the experimental value of the longitudinal elastic modulus E. This point is displaced by a factor 2.27 ± 0.14 above the osmotic pressure line, as is to be expected from the relation $E = c(\partial\pi/\partial c)$.

We now discuss the ratio of E/μ found for the samples in Table I. The samples form two groups: those whose starting concentration is 6% and those of starting concentration 3%. The average ratio of E/μ for the two groups is

$$\text{initially } 6\%: \quad E/\mu = 2.04 \pm 0.17 \qquad (5)$$

$$\text{initially } 3\%: \quad E/\mu = 2.70 \pm 0.27 \qquad (6)$$

For comparison, on the basis of the model gel composed of nonoverlapping coils, one expects this ratio to be 2 in a poor solvent and 3 in a good solvent.[1] The above results imply that the first group of gels is still in the poor-solvent region from the point of view of the Poisson ratio (although the scaling behavior of E characteristic of good-solvent conditions extends up to concentrations some 4 times greater[3] than that of the swollen gels which produced the result 5). Only for the lowest concentrations reported here does the room-temperature measurement of E/μ approach the expected value of 3 in polyacrylamide.

In conclusion, inasmuch as the osmotic properties of gels are concerned, gels and polymer solutions appear to be identical in behavior; the osmotic pressure and the longitudinal elasticity (or at least the osmotic part of it) of the

polyacrylamide gels investigated here do not depend on the history of the sample but only on its concentration. The scaling-law predictions are obeyed.

The shear elastic moduli of the gels reported in this work contrast with the osmotic behavior in that their value depends strongly on their initial concentration and cross-linking density. Even if the concentration dependence of μ upon swelling were linear, as might naively be expected, E/μ would diverge as the gel was deswollen. The observed variation of μ is, however, even slower than predicted, making the apparent divergence even stronger. Only under conditions of equilibrium swelling do E and μ recover their expected ratio.

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Magic-Angle Carbon-13 Nuclear Magnetic Resonance Analysis of the Interface between Phases in a Blend of Polystyrene with a Polystyrene–Polybutadiene Block Copolymer

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ABSTRACT: Magic-angle cross-polarization ^{13}C NMR spectra have been obtained at 15.1 MHz of polystyrene, of random mixtures of polystyrene with perdeuteriopolystyrene, and of a blend of perdeuteriopolystyrene with a polystyrene–polybutadiene block copolymer. Proton $T_{1\rho}$'s (as observed by high-resolution ^{13}C NMR) and intermolecular cross-polarization transfer rates (from protons on one chain to carbons on another) are both dependent on the mixing of protonated and deuterated chains. Results from such independent measures of effective mixing of chains within the deuterated polystyrene–block copolymer blend lead to the conclusion that the interfacial region surrounding the phase-separated rubber domains is unstructured.

Introduction

Adding rubber to polystyrene produces a two-phase material with an impact strength greater than that of polystyrene by itself.[1] The rubber particles imbedded in the polystyrene matrix presumably inhibit macroscopic crack propagation associated with an incipient brittle failure of the polystyrene phase and so improve toughness.[1] Rubber–polystyrene AB block copolymers can also be used to toughen polystyrene. Phillips markets such copolymers under the designation "K-resins". Blending K-resins with polystyrene produces not only a material with good impact resistance but also one which is almost optically clear. The molecular weight of the polybutadiene block of the copolymer determines the rubber particle size. Blended K-resins typically result in dispersed rubber particles too small to be light scattering centers.

A natural question arises as to the nature of the interface between phases when a rubber–polystyrene block copolymer has been blended with polystyrene. Does the polystyrene covalently attached to a rubber particle form a surrounding shell? Or is there some sort of an interfacial gradient from the rubber phase to the polystyrene matrix, a transition which involves the polystyrene chains of the copolymer and provides improved adhesion between the phases?

To answer this question we have used cross-polarization magic-angle[2] ^{13}C NMR to compare mixtures of perdeuteriopolystyrene and polystyrene with a blend of perdeuteriopolystyrene and K-resin. The mixing of polystyrene chains from two sources can be determined experimentally by ^{13}C NMR if chains from one of them are deuterium labeled. In these experiments, proton $T_{1\rho}$'s are obtained from the final slopes of plots of observed carbon magnetization generated by long, matched spin-lock cross-polarization transfers from protons to carbons.[3] A separate proton $T_{1\rho}$ is obtained from each polystyrene-carbon resonance resolved by magic-angle spinning, thereby providing considerably more insight than can be achieved by direct ^1H NMR measurements. These proton $T_{1\rho}$'s are sensitive to spatially dependent proton–proton spin diffusion[4] and so, in a mixture or blend of protonated and deuterated chains, are a measure of the proximity of protonated polystyrene chains with one another. In addition, intermolecular cross-polarization transfers from protons on one chain to deuterated carbons on another chain can be used to characterize the mixing of protonated and deuterated polystyrene chains. The combination of these independent results leads to the conclusion that the interfacial region in the deuterated polystyrene/K-resin blend in fact shows no structural features but rather consists of randomly mixed protonated and deuterated polystyrene chains.

Experiments

Carbon-13 magic-angle experiments were performed at 15.1 MHz, using a Beams-Andrew design rotor (0.7-cm^3 sample volume) and 2-kHz spinning speeds. Matched spin-lock cross-polarization transfers employed H_1's of 44 kHz. Standard radio-frequency pulse sequences and four-phase quadrature routing schemes were used throughout.[5]

Measurements were made on an atactic high-molecular-weight polystyrene (Monsanto), polystyrene-d_8 polymerized from 98 atom % styrene-d_8 (Merck), and mixtures of the two polymers containing 90 and 73 wt % polystyrene-d_8, respectively. Uniform mixtures were made by dissolution of both polymers in chloroform

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