and so forth.

References and Notes

(1) The Langevin forces strictly defined have a covariance matrix proportional to a friction matrix H^{-1}, but the y_i are the random numbers required in a polymer simulation. See ref 2.

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Mechanical Properties of Thermoreversible Atactic Polystyrene Gels

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ABSTRACT: Gels of atactic polystyrene (aPS) in carbon disulfide were formed in the temperature range from 0 to −100 °C. The shear modulus was measured as a function of temperature, concentration, and molecular weight, and a master curve of the data was constructed. The modulus vs. temperature behavior of the aPS gels resembles that of un-cross-linked polymers in the rubbery plateau regime. It is proposed that physical associations act as cross-links and impart elastic properties to the gel network. A molecular weight between associations of 2700 was obtained by using rubber elasticity theory and a simple chain end correction factor for aPS gels of 200 g/L concentration in the plateau region. This defines the minimum molecular weight required for gel formation at this concentration. A more refined statistical approach that accounts for the polymer not included in the network gave a value of 5000. The molecular weight of the chain segment between associations increased as the temperature approached T_{gel} in a manner that was independent of molecular weight.

Introduction

Thermoreversible gels of atactic polystyrene (aPS) can be formed with a variety of solvents.[1] In contrast to thermoreversible gelation of crystallizable polymers, where the crystals themselves act as junctions leading to a network, the subject of a recent review by Keller,[2] none of the current theories concerned with the nature of physical associations involved in network foundation can account for the observed gelation of aPS. Unlike gels of isotactic polystyrene (iPS) and other crystallizable polymers, aPS forms equilibrium gels with equivalent and time-independent gel formation and gel "melting" temperatures.[1,3] The reported heats of formation of 6–26 kJ/mol for aPS gels are significantly lower than 113 kJ/mol observed for iPS gels.[1] Chain entanglements are not required for gel formation since gels can be formed from aPS of molecular weight well below the entanglement molecular weight of polystyrene,[1] although entanglements do appear to increase the stability of aPS gels.[4] Chain overlap is required for gelation, as inferred from the critical gelation concentration for each molecular weight.[1] The shear moduli, approximately 1 kPa, of aPS gels close to T_{gel} are comparable to the moduli of gels formed from crystallizable polymers.[5]

Several authors have discussed the gelation mechanism of aPS solutions. Wellinghoff and co-workers[3] suggested that gels are formed through a microphase segregation process in which finely dispersed polymer domains act as network junction points. "Melting" of the network occurs when the temperature exceeds the T_g of the domains. Tan and co-workers[1] suggested that T_{gel} is not related to T_g since T_{gel} values are in a range 100 °C above the predicted T_g. Two possible gelation mechanisms, chain stiffening and physical associations between chain segments, were hypothesized in this work. Boyer and co-workers[4] related T_{gel} to the fusion flow temperature observed in polymer melts, a $T > T_g$ phenomenon caused by melting of physical associations. These studies give a detailed characterization of the sol–gel transition and have raised interesting questions as to the mechanism by which a stable network of a noncrystallizable polymer can form in solution. In this study of the gel state, the effects of temperature, concentration, and molecular weight on the gel modulus are assessed. The results are compared with the predictions of conventional elastic behavior.

Experimental Section

Narrow disperse aPS ($\overline{M_w}/\overline{M_n} < 1.2$) samples ranging in molecular weight from 2000 to 900 000 were obtained from Pressure Chemical Co. Carbon disulfide (CS_2) was reagent grade and distilled over phosphorous pentoxide prior to use. The freezing point of CS_2 was measured at −110 °C. The concentration of the aPS solutions is given in grams of polymer per liter of solution.

Simple shear tests were performed on gels as a function of temperature, molecular weight, and concentration. Solutions were introduced into a coaxial cylinder instrument shown schematically in Figure 1, and gels were formed in situ by lowering the temperature of the apparatus. Stress–strain measurements were conducted by attaching the inner cylinder to the crosshead of a standard Instron tensile testing device. The outer glass cylinder, a glass vial, remained stationary, while the inner cylinder, a glass rod, was displaced in the vertical direction. A strain rate of 50% per minute was used.

Single-point measurements of the shear modulus were performed by attaching the center cylinder to a modified analytical balance. Loads (0.001–60 g) were applied and deflections approximately of 0.05 mm were measured with a precision of 0.003 mm. Deflections were measured at an elapsed time of 10 s. For this coaxial geometry, the shear modulus, G, is given by

$$G = P \ln (r''/r')/2\pi L x \qquad (1)$$

where P is the load, x is the deflection, L is the depth of the rod in the gel, and r' and r'' are the inner and outer cylinder radii, respectively.[6] The value of $\ln r''/r'$ was 1.64, and L was 17 mm. The temperature of the gel was varied from +25 to −100 °C (±1

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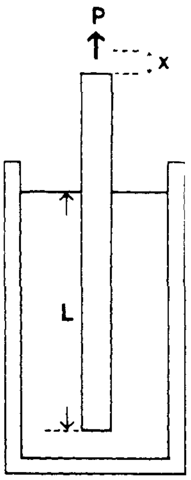

Figure 1. Geometry of coaxial shear apparatus.

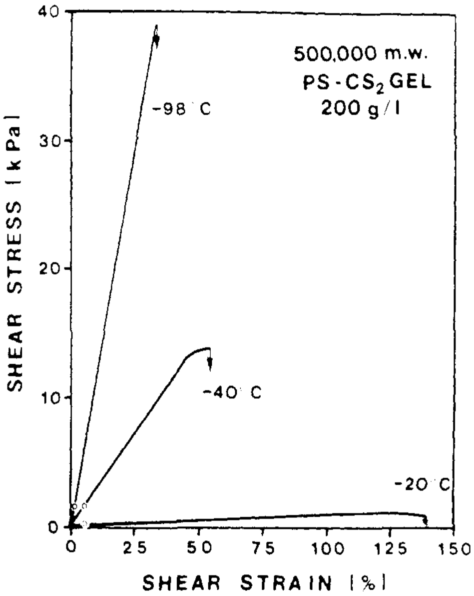

Figure 2. Effect of temperature on the shear stress–strain behavior of 500 000-MW aPS at a concentration of 200 g/L in CS_2.

°C) by a thermostated cooling jacket. Measurements of G were performed by cooling the gel to the desired temperature, allowing the gel to equilibrate for 10 min, and applying the load.

The tensile stress component at the end of the rod was evaluated by measuring G at four different rod depths. The differences among the G values were within experimental error (±5%). It was therefore assumed that this tensile effect was negligible.

Results

The shear stress–strain behavior of a 500 000-MW atactic PS gel at three temperatures below T_{gel} ($T_{gel} = 0$ °C[1]) is shown in Figure 2. The shear modulus, calculated from the initial slope of the curves, increased from 1 kPa at −20 °C to 30 kPa at −40 °C and to 118 kPa at −98 °C. The observed linear deformation to high strains is typical behavior for dilute gels.[7,8] At −98 °C the stress–strain response remained linear up to fracture, while at −40 and −20 °C a yield point was observed at approximately 80% of the fracture strain. Fracture of the gel occurred perpendicular to the glass surfaces near the rod tip. No debonding of the gel from the glass surface was observed.

The single-point shear modulus method was used to examine the effect of concentration and molecular weight on the shear modulus. The stresses and strains measured by this technique are indicated by the circles in Figure 2 to show that they are well within the linear response region of the gels. Modulus values evaluated from the stress–strain curves and the single-point method were identical within experimental error. In Figure 3 are plotted modulus values for 5 concentrations of 500 000-MW aPS in CS_2 as a function of temperature. The modulus–temperature curves are similar in shape for all concentrations. As the temperature decreases below the gel point (as indicated by the solid points on the temperature axis), the modulus increases rapidly over a 40 °C temperature range and then levels off at a value that depends on the concentration. Modulus values below −100 °C were not recorded since the freezing point of CS_2 is −110 °C. Although the shape of the modulus–temperature curves is the same for all concentrations, decreased concentration resulted in reduced modulus values at all temperatures. The lowest concentration examined, 12.5 g/L, is just above the critical gelation concentration of 10 g/L for this molecular weight and solvent.[1]

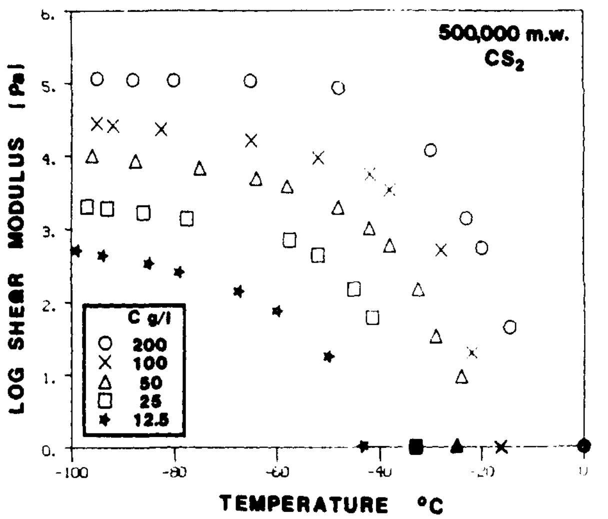

Figure 3. Effect of concentration on the modulus temperature behavior of 500 000-MW aPS gels in CS_2. The solid points indicate the gelation temperature reported by Tan et al.[1]

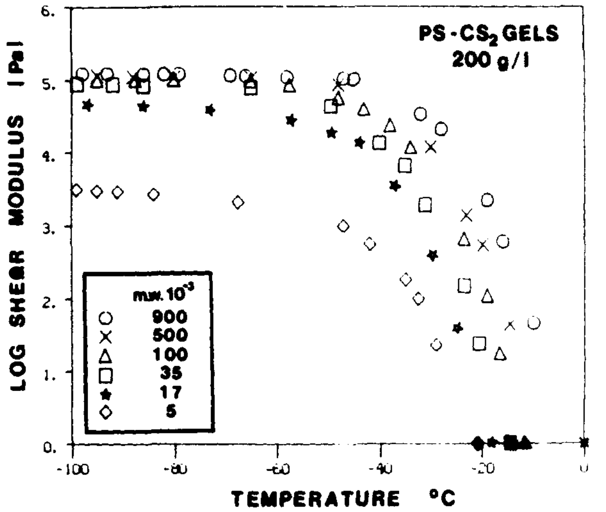

Figure 4. Effect of molecular weight on the modulus temperature behavior of aPS gels with a concentration of 200 g/L in CS_2. The solid points indicate the gelation temperature reported by Tan et al.[1]

The effect of molecular weight on the modulus is shown in Figure 4, where values for six molecular weights at a concentration of 200 g/L are plotted as a function of temperature. Again, the modulus was measured by the single-point method. Qualitatively the curves have the same shape as in Figure 3 and the effect of decreasing

Table I
Comparison of T_{gel} Values

MW × 10^{-3}	concn, g/L	T_{gel},[a] °C	T_{gel},[b] °C
900	200	-5	+15
500	200	-10	0
	100	-15	-18
	50	-20	-24
	25	-27	-30
	12.5	-37	-42
100	200	-12	-12
	100	-32	-32
	50	-52	-54
35	200	-18	-14
	100	-66	-4-
	50	-90	-92
17.5	200	-20	-17
	100	-65	-60
5	200	-23	-21
2	200	no gel	no gel

[a] Extrapolated value from modules-temperature curves. [b] Values from Tan et al.[1]

molecular weight is similar to decreasing concentration. However, molecular weights of 35 000 and higher exhibit virtually the same low-temperature plateau modulus.

Discussion

Tan and co-workers[1] concluded that gelation of aPS in CS_2 is not a glass transition phenomenon but related to a $T > T_g$ process. Boyer and co-workers[4] recently reexamined the data of Tan et al. and suggested a direct correlation between T_{gel} and the fusion flow temperature (T_f) observed in polymer melts.[9] In a qualitative manner, our results reinforce the ideas proposed by Boyer et al. regarding the similarity between the gel state of aPS solutions and the rubbery plateau above the softening temperature. Specifically, we observed a temperature range over which the gel modulus is constant and apparently independent of frequency or rate.[5] The width of the definable plateau depends on molecular weight, and, like the rubbery plateau, as the molecular weight increases, the temperature range becomes broader. It follows that the mechanism of gelation may be similar to that which describes the rubbery plateau as the temperature region, above the softening point, over which physical associations between chains impart elastic properties to the melt. The analogy can be tested by an analysis of the gel modulus measurements using formalism that describes the rubbery plateau region. For this purpose, superposition of the modulus data has been achieved with appropriate shift factors for temperature, concentration, and molecular weight.

All gels exhibit the same limiting modulus at T_{gel} and this was chosen as a reference temperature. Values of T_{gel} were obtained by extrapolation of the modulus–temperature curves in Figures 3 and 4 to zero modulus. As shown in Table I, these values correspond with T_{gel} values obtained by Tan and co-workers[1] except for the highest concentration and molecular weight solutions. These solutions were the most viscous, which appears to influence the experimental determination of T_{gel}. The reduced temperature is defined as

$$T_r = T/T_{\text{gel}} \tag{2}$$

where T_{gel} is the extrapolated gelation temperature.

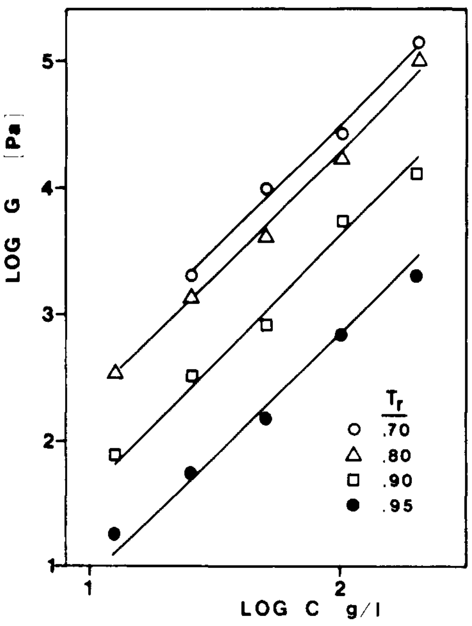

Figure 5. Relationship between modulus and concentration for 500 000-MW aPS at four reduced temperatures.

Table II
Values of the Concentration Shift Factor

concn, g/L	$(\rho/c)^2$
1040 (bulk)	1.00
200	27.0
100	108
50	432
25	1730
12.5	6920

Table III
Plateau Modulus Values and the Molecular Weight Shift Factor, *b*, Measured at T_r = 0.7 and c = 200 g/L

MW × 10^{-3}	G, kPa	b
900	120	1.00
500	110	1.09
100	101	1.19
35	89	1.35
17.5	60	2.00
5	3	40.0

The relationship between modulus and concentration is examined in Figure 5, where log G vs. log concentration (C) is plotted. The modulus values were obtained from the modulus–temperature curves in Figure 3 at four reduced temperatures, including both the rapid rise and plateau regimes. The slope of 2 defines a squared dependency of modulus on concentration over the entire temperature range. Numerous examples of this dependency have been observed for plasticized polymers in the rubbery plateau regime and for other thermoreversible polymer gels.[10–13]

Modulus values are shifted by a factor

$$(\rho/c)^2 \tag{3}$$

where ρ is the polymer density.[14] Values of this factor at several concentrations are listed in Table II to show that very large shift factors are necessary for the lowest concentrations. The same values were used for all molecular weights.

The dependence of modulus on molecular weight was evaluated empirically from the modulus–temperature curves in Figure 4. The plateau modulus value for each molecular weight was shifted by a factor b to coincide with the plateau value for the highest molecular weight (900 000). The shift factor b is defined as

$$b = G°/G \tag{4}$$

where $G°$ is the plateau modulus for 900 000-MW aPS. The same value of b, given in Table III, was used for all

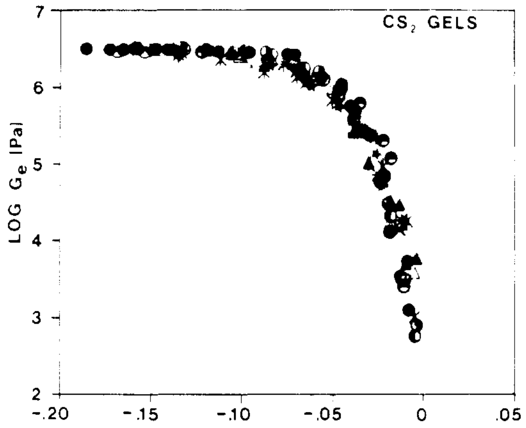

Figure 6. Master curve of all aPS/CS_2 gel modulus temperature data. Concentrations and molecular weights examined are given in Table I.

Table IV
Effect of Molecular Weight on the Plateau M_a Values Measured at T_r = 0.74 for 200 g/L aPS Gels

MW × 10^{-3}	M_a × 10^{-3}
900	2.6
500	2.8
100	2.8
35	2.8
17.5	3.2
5	2.4

concentrations of a given molecular weight.

The shift factors defined above were used to construct a master curve of all the modulus–temperature data. The effective modulus, G_e, is defined as

$$G_e = G(\rho/c)^2 b \tag{5}$$

where G is the observed modulus. In Figure 6 is plotted log G_e as a function of log T_r. This master curve represents the modulus–temperature relationship for gels of 900 000-MW aPS with no solvent. The plateau modulus of 3 × 10^6 Pa is close to the 10^5 to 10^6 Pa range for aPS in the rubbery plateau region[15] and is significantly below the 10^9 Pa modulus of aPS in the glassy state.[16]

For an ideal rubber the modulus should depend only on the molecular weight of the chain between junctions, which for gels is the molecular weight M_a between the associations that constitute the junctions, and should only be affected by the molecular weight of the initially un-cross-linked chain (M) in as far as there are free chain ends that do not contribute to the network. Consequently, the shift factor b should be an expression of this free chain end effect. It follows that b should be increasing for decreasing M because the unjoined end portion of the chain becomes a larger fraction of the total material. This in fact is the trend displayed by Table III.

In what follows we shall test the above using first the simplest expression for the modulus in the theory of rubber elasticity[14]

$$G = \frac{cRT}{M_a}\left(1 - \frac{2M_a}{M}\right) \tag{6}$$

If eq 6 is obeyed, M_a should be independent of M and the chain-end correction factor (1 − $2M_a/M$) should be equivalent to the inverse of the shift factor b. Table IV shows that M_a is indeed largely invariant with M for a T_r value corresponding to the plateau region except for the lowest M values. Since the average value of 2700 is considerably smaller than the calculated entanglement molecular weight of 175 000 for this concentration[4] it is apparent that the physical associations that form the gel network are not entanglements. The calculation of M_a also suggests a lower molecular weight limit for gelation of aPS and this was subsequently confirmed by our observation that a 200 g/L solution of 2000-MW aPS did not form a gel when cooled to −100 °C. The effect of concentration on the low-temperature plateau value of M_a is given in Table V and shows the expected inverse proportionality.

Table V
Effect of Concentration on the Plateau M_a Values Measured at T_r = 0.74 for 500 000-MW aPS Gels

concn, g/L	M_a × 10^{-3}
200	2.8
100	6.7
50	8.5
25	18.2
12.5	30.9

Table VI
Comparison of the Modulus Correction Factors

MW × 10^{-3}	b^{-1}	(1 − $2M_a/M$)	y^a
900	1.00	0.994	0.989
500	0.92	0.989	0.980
100	0.84	0.946	0.900
35	0.74	0.845	0.715
17.5	0.50	0.691	0.475
5	0.025	−0.080	0.104

[a] Evaluated for M_a' = 5000.

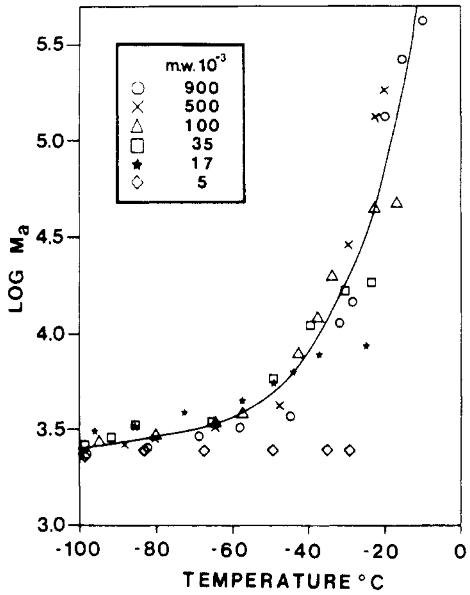

Figure 7. Effect of temperature on M_a for six aPS gels of different molecular weights at a concentration of 200 g/L.

The temperature dependence of M_a determined in this way is plotted in Figure 7. For all but the lowest M's, M_a increases rapidly with T. This of course is a direct reflection of the rapidly decreasing modulus. In terms of rubber theory it would correspond to the gradual melting out of associations, leaving behind increasingly larger network chains, for which Figure 7 provides a quantitative estimate. Also the data for the different M's superpose as they should if M_a is independent of molecular weight. The worsening fit for the lower M's arises from the increasing inapplicability of the chain-end correction in eq 6.

The last point is brought out by Table VI, which suggests that the molecular weight dependence is more complex than represented by eq 6, which simply considers two free ends for each initially unlinked chain. In what follows this molecular weight dependence will be refined through a statistical approach taking account of the amount of polymer not forming part of the gel network.

The model is given below. Molecules with zero or one association do not contribute to the network modulus. Molecules with two or more associations do contribute except for the two ends of such molecules. With n associations, there are $n + 1$ sections on a molecule and $n - 1$ of these are part of the network. This approach, using the hypothesis of random placement of associations along the chain, follows Poisson statistics. The fraction of polymer mass for monodisperse polymer that does not participate in the network (F) can be written as

$$F = e^{-a}(1 + a) + e^{-a}\sum_{2}^{\infty}\frac{a^n}{n!}\,\frac{2}{n + 1} \qquad (7)$$

where $a = M/M_a'$, the average number of associations in the molecule of molecular weight M. Equation 7 can be readily summed. The fraction of polymer mass that is part of the network, y, is then expressed in eq 8. When the

$$y = 1 - 2/a + e^{-a}(1 + 2/a) \qquad (8)$$

statistical approach is compared to the average approach in its correlation with b^{-1}, Table VI, the statistical approach is significantly better. The best correlation between y and b^{-1} was found with $M_a' \simeq 5000$. This low-temperature plateau value of M_a' is quite different from the value of M_a found with the average approach (2700). Calculated values of G (eq 6) using M_a' would be about half of the measured ones.

The discrepancy between M_a and M_a' may be a result of the simplistic assumption that the gel network structure is the same as in cross-linked rubbers. The structure of gels is not necessarily homogeneous and may contain interconnected micellar regions.[3] These may act as high-functionality junction points that do not contribute to the deformation of the network. This is similar to the effect of polystyrene domains in thermoplastic elastomers and crystallites in polyurethanes.[17,18] In these materials, plateau modulus values are higher than predicted and the segmental length may be underestimated by a factor of 2–4.[19]

The modulus expression (eq 6) was modified for the discrepancy between M_a and M_a' by addition of a factor of 2 and the chain-end correction was replaced by y (eq 8) to give

$$G = 2cRTy/M_a' \qquad (9)$$

Values of M_a' were determined from the modulus data for gels of six molecular weights at 200 g/L concentration and are plotted as a function of temperature in Figure 8. Comparison to the M_a data in Figure 7 shows that much better superposition is achieved with M_a', particularly in the region of T_{gel}, even if some discrepancy for the material with the lowest M still remains. The values of M_a' are always higher than M_a, and M_a' may exceed the molecular weight of the polymer. Some fraction of the polymer mass is not incorporated into the gel network and may be considered sol; this is in accord with the assumptions of the statistical approach.

Conclusions

1. The present results thus reveal that the aPS gels in this study display rubber elastic properties in all those respects that have here been examined. This includes the existence of the "rubbery" plateau in the modulus.

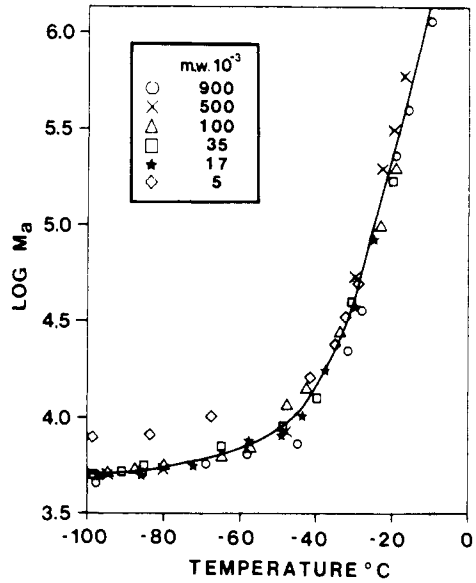

Figure 8. Effect of temperature on M_a' for six aPS gels of different molecular weights at a concentration of 200 g/L.

2. The modulus values scale with the square of the concentration and show a dependence on the initial unjoined molecular weight such as can be attributed to free chain ends for all except the shortest chains. This correspondence to rubber elasticity is not altogether unexpected if one recalls that traditionally the network theories are tested on swollen rubbers that are in fact equivalent to our gels except for the permanence of the junctions, the function of the swelling medium being to reduce interchain interactions, which thus allows the entropic behavior of the individual chains to prevail. The present results therefore encourage further measurements on thermoreversible aPS gels along the lines adopted in conventional rubbers.

3. Beyond demonstrating consistency with rubber elastic network behavior, possibly the most significant conclusion is the estimate of the molecular weight of chain segments between the junctions based on rubber theory. Even if there is a factor of 2 difference (2700 vs. 5000) between values obtained by the conventional and a new more refined approach for the chain-end corrections, these values provide pointers to the nature of the junctions: they exclude the possibility of conventional entanglements, suggesting specific physical associations.

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Registry No. aPS (homopolymer), 9003-53-6.

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Correctly Averaged Non-Gaussian Theory of Rubberlike Elasticity. Application to the Description of the Behavior of Poly(dimethylsiloxane) Bimodal Networks

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ABSTRACT: A new theoretical relationship between the rubberlike elasticity of a polymer network and the distribution of the vector connecting junction points (or the end-to-end vector distribution function of the chain joining two of these points) is presented. In this approach the free energy of the chains is correctly averaged over the network structure, a difference with respect to older treatments in which a preaveraged deformation dependence is considered. The new theory and a slight modification in the previous procedure to analyze bimodal network data lead to a more satisfactory explanation of these data (presenting a pronounced upturn for high extensibilities due to non-Gaussian effects) in terms of molecular magnitudes.

Introduction

In a recent work,[1] some of us presented a method to relate the elastomeric properties of polymer networks with the chain length distribution. This method makes use of an analytical form for the end-to-end distance distribution function, $F(R)$, or the spherically symmetric part of the end-to-end vector distribution function, $F(\mathbf{R})$, in terms of coefficients determined by inference from the even moments $\langle R^{2p}\rangle$. ($\mathbf{R}$ represents the vector joining two connected junction points in the network structure, referred to a local system associated to the chain joining these points, and the broken brackets represent both orientational and conformational average with respect to an external system or the network structure.) Simultaneously, Mark and Curro[2,3] published a series of papers in which they approach the same problem through Monte Carlo generated distribution functions. Both types of theoretical calculations have an obvious experimental reference: the data corresponding to bimodal networks composed by short and long chains, for which an important deviation with respect to the behavior associated to a simple Gaussian distribution is clearly observed at high elongations,[4,5] so that a pronounced upturn in the stress–strain curves is shown, due to the limited flexibility of the short chains. However, the agreement between numerical calculations based in non-Gaussian theories and experimental data is only qualitative. In our opinion, there are two main problems from which the quantitative discrepancies may arise:

First, the theoretical relationship between elastic forces and distribution functions proposed in previous works[1–3] is based in an expression for the free energy in terms of the preaveraged end-to-end vector of the chain connecting two junction points

$$A(\alpha) = -k_B T \ln F[\langle(\alpha\cdot\mathbf{R})^2\rangle^{1/2}] \qquad (1)$$

where $F(\mathbf{R})$ is the actual distribution function of the fixed end-to-end points (cross-links). α is the deformation tensor. For practical purposes (see the next section) we define the radial distribution function in the usual manner

$$W(R) = 4\pi R^2 F(R) \qquad (2)$$

The argument in the distribution function in eq 1 is the deformed and averaged end-to-end vector

$$\langle(\alpha\cdot\mathbf{R})^2\rangle = \sum_{i=1}^{3}\alpha_i^2\langle R_i^2\rangle = (\langle R^2\rangle/3)\sum_{i=1}^{3}\alpha_i^2 \qquad (3)$$

which gives the characteristic deformation dependence.

If $F(\mathbf{R})$ is a simple Gaussian function of R, we find from eq 1 and 3 the free energy for the Gaussian network $A = (1/2)k_B T\sum_{i=1}^{3}\alpha_i^2$. (If we would have allowed the cross-links to fluctuate in the James and Guth sense the only change would be a factor $^1/_2$ in the modulus.)

However the correct expression for the free energy is[6]

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