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(18) When two sufficiently long chains react, they may be linked in three ways: (i) end-to-end, thus forming a longer chain; (ii) end-to-nonterminal unit, thus creating a trifunctional branch point; (iii) nonterminal unit to nonterminal unit, thus forming a tetrafunctional branch point. Our assumption of a most probable distribution of primary chains implies that branch points are tetrafunctional. Pla calculated the branching probabilities based on trifunctional branch points from the measured "*g* factors" in the sol fraction of dioxane lignin.[26] We recalculated, from the same *g* factors, these probabilities based on tetrafunctional branch points. The relationships between branching probability and the *g* factor are given by Zimm and Stockmayer (Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301).
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Volume Dependence of the Elastic Equation of State. 2. Solution-Cured Poly(dimethylsiloxane)

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ABSTRACT: Vapor sorption measurements for solution-cured poly(dimethylsiloxane) + cyclohexane are reported. The Flory–Huggins interaction parameter χ is found to be $\chi = 0.433 - 0.010v_2$, where v_2 is the volume fraction of polymer. Differential solvent vapor sorption by cross-linked and un-cross-linked PDMS is reported as a function of volume fraction of solvent in the cross-linked PDMS. The elastic component of the solvent chemical potential is investigated as a function of the degree of dilation. Qualitative differences between bulk-cured and solution-cured samples are apparent, and Flory's recent theory of rubber elasticity accounts qualitatively for this behavior.

Introduction

The behavior of solvent-swollen elastomers is dependent upon the thermodynamics of both the mixing process and the elastic restoring forces. If one assumes, with Flory,[1] that these two contributions to the free energy are additive, it follows that the chemical potential of the diluent consists of additive contributions and that the thermodynamic activity of the diluent is the product of two separable components. If $a_{1,c}$ and $a_{1,u}$ represent, respectively, the activities of solvent in cross-linked and un-cross-linked, but otherwise identical polymers, then the ratio $a_{1,c}/a_{1,u}$ at equal polymer volume fractions is the elastic contribution to the solvent activity. Accordingly, this ratio of activities should be comprehensible solely in terms of the elastic equation of state.

Experiments to test this prediction were conducted some years ago by Gee, Herbert, and Roberts[2] on natural rubber (NR) + benzene and more recently by Yen and Eichinger[3] on poly(dimethylsiloxane) (PDMS) + benzene, poly(styrene-*co*-butadiene) (SBR) + benzene, and SBR + *n*-heptane. In all cases the quantity $\lambda \ln (a_{1,c}/a_{1,u})$ exhibits a maximum when plotted against λ^2, where $\lambda^3 = (V/V_0)$ is the ratio of the volume V of the isotropically swollen elastomer to the dry volume V_0 (swelling ratio). The magnitude of the maximum appears to be system dependent, but the fact of its presence in the four systems investigated to date can scarcely be questioned.

The authors of the experiments cited above were unable to account for this result with conventional theories of elasticity and resolved that the assumed additivity of contributions to the free energy was questionable. This conclusion was rejected by Flory,[4] who showed that the swelling behavior is encompassed by his treatment of the constraints which act to limit the range of configurations available to cross-linkages. He predicted that if experiments were performed with solution-cured polymers, their behavior would be qualitatively different from that observed with the bulk-cured samples that had preoccupied the previous investigators.

With the urging and assistance of Professor J. E. Mark, we have undertaken a series of measurements to test this prediction.

Experimental Section

Polymer. The poly(dimethylsiloxane) (PDMS) used for this study was kindly supplied by Professor J. E. Mark. The un-cross-linked polymer contains 0.5 mol % (methylvinyl)siloxane

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units and has a molecular weight of approximately 500 000. A sample was prepared for measurements by fractionation from a 1% solution in cyclohexane, with acetone as the precipitant. The first two small fractions were discarded, and a third was retained for use as un-cross-linked samples.

A wide range of cross-linked PDMS elastomers has been prepared and characterized by Mark and colleagues.[5-8] The sample designated by them as S4-9 was selected for this study; it had been cross-linked in a 48% by volume polymer solution by irradiation with 19.3 Mrd of γ radiation from a ^{60}Co source. The gel volume fraction at cross-linking conditions is 0.457 when corrected for the soluble (or sol) fraction of the sample; equilibrium swelling in cyclohexane at 25 °C occurs at 0.159 volume fraction of polymer.[5]

The densities of cross-linked and un-cross-linked polymer samples were assumed to be unaffected by the presence of either cross-linkages or methylvinyl groups. Shih and Flory[9] report the density of PDMS at 30 °C to be 0.9653 g/cm^3, which we have used for reducing our measured masses to volume fractions.

Solvents. Spectrophotometric grade cyclohexane (Aldrich) and reagent grade acetone were used for fractionation without further purification.

Cyclohexane from the same lot was used for measurements in the vapor sorption apparatus to be described. It was partially purified in situ by several freeze–pump–thaw cycles. The density of cyclohexane at 30 °C is reported[10a] to be 0.7693 g/cm^3, and its vapor pressure[10b] is 121.786 torr.

Apparatus and Method. The vapor sorption apparatus has been previously described.[3] It consists of a quartz spring balance for integral sorption measurements and a Cahn Model RG electrobalance for differential measurements. Un-cross-linked samples weighing ca. 30 mg were uniformly coated onto aluminum pans (10-mm diameter and 30-μm thickness) by solvent evaporation. One of these samples was suspended from the quartz helix, and the other was counterbalanced with a similar mass of cross-linked sample S4-9 on the vacuum electrobalance.

The thermostated temperature of the water surrounding the sorption apparatus was controlled at 30.003 ± 0.005 °C. Cyclohexane vapor was admitted from its reservoir in increments as determined by the reservoir temperature. The system was allowed to equilibrate after each addition of vapor until readings taken at intervals of 12 h became constant. Vapor pressures were determined by means of a mercury manometer read with a cathetometer. Corrections for unequal crown heights were applied as needed.[11] The extension of the quartz helix (1.02 ± 0.01 mm/mg) was likewise determined with the cathetometer. The output from the Cahn electrobalance was displayed on a strip chart recorder (Honeywell Electronik 194). Apparent mass differences recorded with the electrobalance were corrected for unequal balance arm lengths according to careful calibration.

Measurements were made after each one of a half-dozen or so successive additions of cyclohexane vapor, whereupon the system was evacuated to ensure against cumulative errors arising from a slow leak. (The vacuum system was judged to be unsatisfactory if there was a leak in the evacuated system that could be observed with a McLeod gauge in a 24-h period.) Several such runs were made and never was any hysteresis observed.

Results and Discussion

The Flory–Huggins interaction parameter χ was calculated according to

$$\ln a_1 = \ln (1 - v_2) + v_2 + \chi v_2^2 \tag{1}$$

where a_1 is the activity of the solvent and v_2 is the volume fraction of polymer. Results for the PDMS + cyclohexane system are shown in Figure 1. The triangles are representative osmotic results of Kuwahara, Okazawa, and Kaneko[12] at 20 °C. The solid line is a least-squares fit through our data (squares) at high concentrations and Kuwahara et al.'s at low concentration. The equation for the solid line is

$$\chi = 0.433 - 0.010 v_2 \tag{2}$$

No correction has been applied to reduce the osmotic data to 30 °C, for reasons to be mentioned shortly.

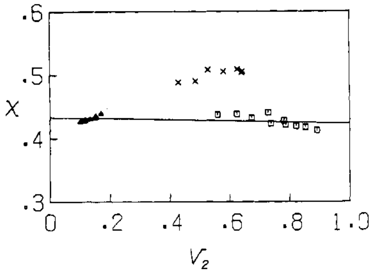

Figure 1. Measured Flory–Huggins interaction parameter χ as a function of the volume fraction v_2 of PDMS in cyclohexane. Squares, our vapor sorption data at 30 °C; triangles, osmotic data of Kuwahara et al.[12] at 20 °C; crosses, vapor sorption data of Shih and Flory[13] at 25 °C.

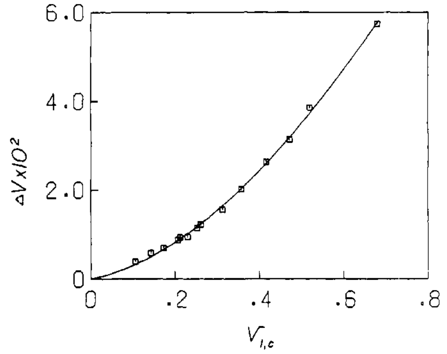

Figure 2. Volume fraction difference vs. volume fraction of cyclohexane in the cross-linked PDMS at 30 °C.

Some of the data points at the high and low ends of our measured concentration range were omitted from the least-squares analysis; they are subject to large errors owing either to the small solvent mass absorbed or to activities approaching unity. The propagated error in our measured χ ranged from ±0.005 at high concentration to ±0.01 at low concentration.

Shih and Flory[13] have also measured χ for this system at 25 °C. Their osmotic measurements are in good agreement with those of Kuwahara et al.[12] and are not shown. However, their vapor sorption measurements, shown as crosses in Figure 1, differ from ours by approximately 18%. Delmas, Patterson, and Bhattacharyya[14] measured the heat of mixing ΔH_M^∞ of PDMS to infinite dilution in cyclohexane at 25 °C; they obtained $\Delta H_M^\infty = 5.2$ J g^{-1}. This measurement, coupled with the close agreement between osmotic pressure data at 20 and 25 °C, demonstrates that the enthalpy of mixing for this system is not large and, hence, that activities at 30 °C would not differ from those at 20 °C by an amount exceeding experimental errors.

The differences in solvent mass absorbed by the un-cross-linked PDMS and cross-linked PDMS at equal solvent activities were converted into Δv, defined as $v_{1,u} - v_{1,c}$, where subscripts u and c refer, respectively, to un-cross-linked and cross-linked PDMS. Experimental results are shown in Figure 2. The solid curve in Figure 2 is a third-degree polynomial least-squares fit which is constrained to pass through the origin; its equation is

$$\Delta v = 0.0194 v_{1,c} + 0.1155 v_{1,c}^2 - 0.0275 v_{1,c}^3 \tag{3}$$

The data could also be fit with the following similarly constructed and constrained second-degree polynomial:

$$\Delta v = 0.0242 v_{1,c} + 0.0905 v_{1,c}^2 \tag{4}$$

It was judged that differential and integral mass data in the low polymer concentration range were accurate,

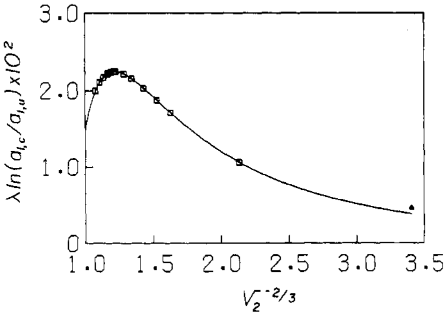

Figure 3. Plot of λ ln $(a_{1,c}/a_{1,u})$ vs. $v_2^{-2/3}$ as a smooth function for PDMS + cyclohexane at 30 °C. The triangle represents the swelling equilibrium point.[5]

while activity measurements in this range were not. Activity measurements approach unity in this range, where the quantity of interest, ln a_1, can be approximated as

$$\ln a_1 = \ln [1 - (1 - a_1)] \simeq -(1 - a_1) \qquad (5)$$

The difference between the activity and unity becomes the important quantity for low polymer concentrations, which subjects chemical potentials to large relative errors. The errors in the differential and integral mass measurements, however, remained nearly constant throughout the concentration range studied. Differential mass data in the low polymer concentration range have been included in Figure 2. These data in the low polymer concentration range become useful when coupled with interpolated values of χ from eq 2. The activity data may be represented by combining eq 1 and 2 in the form

$$a_1 = v_{1,u} \exp[v_{2,u} + (0.433 - 0.010 v_{2,u}) v_{2,u}^2] \qquad (6)$$

Equation 6 is the best fit of present activity data, exclusive of the Shih and Flory[9] vapor sorption data, over the entire range of polymer composition.

The ratio $a_{1,c}/a_{1,u}$, at equal polymer volume fractions was calculated by combining the data from Figures 1 and 2; this procedure will now be illustrated. An arbitrary $v_{1,c}$ is assumed; from Figure 2 or either eq 3 or 4, Δv is obtained and $v_{1,u}$ is determined through addition. The quantities $v_{1,c}$ and $v_{1,u}$ represent the solvent volume fractions in the cross-linked and un-cross-linked PDMS samples at equal solvent activities, respectively. Substitution of $v_{1,u}$ into eq 6 yields $a_{1,c}$. The ratio $a_{1,c}/a_{1,u}$ at an equal polymer volume fraction is desired; thus $v_{1,c}$ is substituted for $v_{1,u}$ in eq 6 and $a_{1,u}$ is obtained.

The derived values of λ ln $(a_{1,c}/a_{1,u})$ have been plotted against $v_2^{-2/3}$ in Figure 3. For a polymer cross-linked in solution, Flory[15] showed that

$$\lambda = (v_2^0/v_2)^{1/3} \qquad (7)$$

where v_2^0 is the volume fraction of polymer when cross-linked. Figure 3 contains the results obtained by using the third-order fit to Δv; the second-order fit to Δv yields similar results. The solid line in Figure 3 was generated following the above procedure by assuming values of $v_{1,c}$ ranging from 0.001 to 0.841. Our smoothed experimental points are represented as squares. The swelling equilibrium point is calculated from

$$\ln (a_{1,u}/a_{1,c}) = \ln (1 - v_{2,s}) + v_{2,s} + \chi v_{2,s}^2 \qquad (8)$$

where $v_{2,s}$ is the volume fraction of cross-linked polymer at swelling equilibrium as determined by Mark and coworkers[5] and χ is obtained by interpolation with use of eq 2; the triangle in Figure 3 represents this point. (The swelling equilibrium datum was not included in the polynomial fits given in eq 3 and 4.) From Figure 3, λ ln $(a_{1,c}/a_{1,u})$ exhibits a maximum when plotted against $v_2^{-2/3}$.

Table I

system	maximum location $v_2^{-2/3}$	cure type
NR + benzene[2]	1.8	bulk
PDMS + benzene[3]	1.5	bulk
SBR + benzene[3]	1.8	bulk
SBR + *n*-heptane[3]	1.6	bulk
PDMS + cyclohexane	1.2	solution

(Note that $v_2^{-2/3}$ is essentially λ^2 with the $(v_2^0)^{2/3}$ factor excluded. The effect of plotting versus λ^2 would be to shift the abscissa scale to the right.) Thus, a maximum appears in all systems studied to date, both solution cured and bulk cured. Table I contains a summary of these systems, the locations of their maxima, and the network cure type. The maximum for the solution-cured sample occurs at a lower dilation than any of the bulk-cured samples studied previously. There is an obvious qualitative difference between bulk-cured and solution-cured samples, exclusive of any latent solvent dependence.

Analysis Using Flory Theory

Through consideration of the constraints on junctions in real networks, Flory has shown[15]

$$\lambda \ln (a_{1,c}/a_{1,u}) = (\xi V_1/V^0)[1 + (\mu_j/\xi)K(\lambda)] \qquad (9a)$$

where μ_j is the number of junctions, ξ is the cycle rank of the network, V_1 is the molar volume of the diluent, V^0 is the network volume in the reference state, and

$$K(\lambda) = \dot{B}/(1 + B^{-1}) + \dot{D}/(1 + D^{-1}) \qquad (9b)$$

$$\dot{B} \equiv \partial B/\partial(\lambda^2) \qquad (9c)$$

$$\dot{D} \equiv \partial D/\partial(\lambda^2) \qquad (9d)$$

$$B = \kappa(\lambda^p + \kappa)^{-2}[\kappa(\lambda^2 - 1) - \lambda^p + \lambda^2] \qquad (9e)$$

$$D = \kappa(\lambda^p + \kappa)^{-2}\lambda^p[\lambda^p + \lambda^{-2}(\lambda^p + \kappa) - (2 + \kappa\lambda^{-p})] \qquad (9f)$$

The equations for B and D are corrected versions of those presented by Flory.[15] For a perfect tetrafunctional network $\mu_j = \xi$ and $1 + K(\lambda)$ becomes proportional to $\lambda(\mu_1 - \mu_1{}^\circ)_{\mathrm{el}}$. The factor $1 + K(\lambda)$ will be used in the following calculations. In the above equations, p expresses the dependence of the domain of entanglement constraints on the strain. This is seen by expressing the a priori probability, $P(\Delta x_t)$, for a displacement Δx_t from the center of constraint in the direction of the t axis as[4]

$$P(\Delta x_t) = (\text{constant}) \exp[-\kappa\rho\lambda_t^{-p}(\Delta x_t)^2] \qquad (10)$$

Here $\rho = 3/2\langle(\Delta R)^2\rangle$ is the parameter that characterizes the (Gaussian) fluctuations ΔR of the junctions from their mean positions in the phantom network and

$$\kappa = \langle(\Delta R)^2\rangle/\langle(\Delta S)^2\rangle_0 \qquad (11)$$

measures the severity of constraints exerted by neighboring chains relative to those imposed by the network of phantom chains. To obtain eq 9e and 9f we have retained the dependence of the a priori probability on the strain as $\sigma_{0x} = \sigma_0\lambda_x^{-2}$ in evaluating the contribution from the alteration of $S_*(\Delta x)$ to the elastic free energy,[15] but have otherwise replaced λ^{-2} by λ^{-p} as in eq 10.

The above formulation is illustrated through calculations shown in Figure 4. A polymer volume fraction at cure of 0.457, equal to that of the PDMS sample tested, was assumed for all calculations. In Figure 4, $1 + K(\lambda)$ is plotted against $v_2^{-1/3}$ at values of p equal to 3 (dashed line) and 4 (solid line) for the values of κ shown. At $p = 2$, the curves generated from the above theory do not exhibit a maximum. Two general trends can be seen from these curves. First, as p is increased, the maximum becomes more

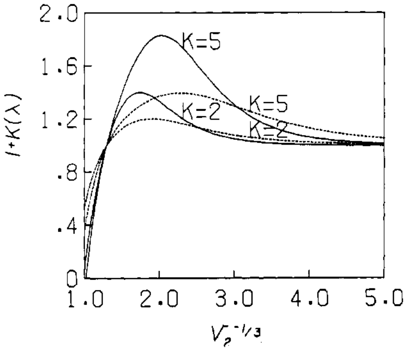

Figure 4. Calculations of $1 + K(\lambda)$ vs. the linear dilation ratio $v_2^{-1/3}$ for networks formed at a volume fraction 0.457. For the solid curves $p = 4$, and for the dashed curves $p = 3$; values of κ are given with each curve.

prominent, and second, as κ is decreased (p constant), the maximum occurs at smaller dilutions.

While a quantitative correspondence between Figures 3 and 4 cannot be made, the striking qualitative similarity between the experimental and theoretical curves cannot be denied. As Flory[4] has shown, the theoretical elastic equation of state reflects a transition between two extremes of behavior. At small strains the entanglement constraints predominate and the junction displacements approach affine behavior. At higher strains the entanglement constraints become less severe, and the behavior deduced by James and Guth[16] for phantom networks is approached.

Conclusions

This work verifies that the elastic contribution to the chemical potential of the diluent in a solution-cured network is encompassed, qualitatively at least, by Flory's[4,15] recent theory of rubber elasticity. The separation of mixing and elastic contributions to the free energy of swollen elastomers now seems to be less questionable than it was in the earlier work. Further swelling measurements to test the implications of the theory are currently being undertaken.

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Effect of Polyelectrolyte Charge Density on Calcium Ion Activity Coefficients and Additivity in Aqueous Solutions of Calcium Acrylamide–Acrylic Acid Copolymers

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ABSTRACT: Calcium ion activity coefficients have been determined in aqueous solutions of fully neutralized calcium poly(acrylamide–acrylic acid) copolymers whose charge spacing ranged from 3.9 to 25 Å. Measurements were made at 25 °C in both the absence and the presence of added simple electrolyte, $CaCl_2$. In the absence of $CaCl_2$, the activity coefficients are shown to decrease linearly with the square root of the polyelectrolyte charge density and are shown to obey an empirical expression relating the measured activity coefficients to the counterion charge and polyelectrolyte charge density. In the presence of $CaCl_2$, the measured activity coefficients are in excellent agreement with those predicted by an additivity of contributions from the simple salt and polyelectrolyte.

Introduction

There are few systematic investigations in which the charge density of the polyelectrolyte is varied while the chemical nature of the backbone is kept constant.[1-8] Such studies aimed at understanding the interactions of monovalent and multivalent counterions with polyelectrolytes are of paramount importance. Recently, it was reported that in salt-free solutions of fully neutralized sodium acrylamide–acrylic acid copolymers a linear relationship between the measured counterion activity coefficients γ_{Na^+} and the polyion charge density was observed[5]

$$\gamma_{Na^+} = I - S\xi^{1/2} \tag{1}$$

where ξ is the dimensionless charge density parameter commonly used to characterize polyelectrolytes

$$\xi = e^2/DkTb \tag{2}$$

with e being the protonic charge, D the bulk dielectric constant, k the Boltzmann constant, T the absolute temperature, and b the average spacing of ionic groups along