Macromolecules **1982**, *15*, 531–535

properties of a switchboard model of a polyethylene chain and shown that it leads to a density of 2.4 g/cm^3 for the amorphous phase for chains with no tilt or, conversely, that a tilt of 70° to the normal is required in order to achieve the density that is normally accepted for the polyethylene amorphous phase. Neither such densities nor such tilts have ever been observed in linear polyethylene under normal crystallization conditions. This calculation shows the unphysical character of the switchboard model. The density excess can be eliminated by chain folding within the crystal.

Acknowledgment. We thank Dr. John D. Hoffman for his many stimulating discussions and helpful comments and ideas on the paper.

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Volume Dependence of the Elastic Equation of State. 3. Bulk-Cured Poly(dimethylsiloxane)

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Received November 2, 1981

ABSTRACT: Vapor sorption measurements for bulk-cured poly(dimethylsiloxane) + cyclohexane and benzene are reported. The Flory–Huggins interaction parameter χ for the cyclohexane system is found to agree, within experimental error, with our previously reported data for this system. For the benzene system, χ is, within experimental error, identical with the results of Shih and Flory. Differential solvent vapor sorption by cross-linked and un-cross-linked PDMS is reported, and the elastic component of the solvent chemical potential is investigated as a function of the degree of dilation for both systems. Comparisons are made between the bulk- and solution-cured PDMS + cyclohexane systems. Results are found to be in quantitative agreement with the current form of Flory's elasticity theory. However, the data demonstrate that the mixing and elastic free energies are not strictly separable.

Introduction

In a previous paper[1] we presented swelling data for a solution-cured poly(dimethylsiloxane) (PDMS) sample with cyclohexane and demonstrated that the elastic component of the solvent chemical potential was qualitatively encompassed by Flory's recent theory[2,3] of elasticity. We concluded that the Flory–Rehner assumption[4,5] of separability of the elastic and mixing free energies in a swollen polymer network was less questionable than had been deduced from earlier work.[6,7] Here we report data for bulk-cured PDMS + cyclohexane and benzene, in which the same PDMS elastomer was used in both runs. Comparisons are also made between the bulk-cured and solution-cured PDMS when swollen with cyclohexane.

According to the theory elaborated by Flory and coworkers,[2,3,8] the elastic contribution to the solvent chemical potential, $\mu_{1,\mathrm{el}}$, is given by

$$\lambda\mu_{1,\mathrm{el}}/V_1 = f(\lambda^2) \tag{1}$$

where $\lambda = (V/V^0)^{1/3}$ is the extension ratio and V_1 the solvent molar volume. If the Flory–Rehner[4] assumption of separability is combined with the James–Guth[4] theory, $f(\lambda^2)$ = const, but if instead the Wall–Flory[5] elastic equation of state is used, $f(\lambda^2)$ is a monotonically increasing function of λ^2. According to the elasticity theory one adopts, $f(\lambda^2)$ departs from constancy to the extent that the chosen theory departs from the James–Guth isotherm, but for any case the Flory–Rehner assumption gives $f(\lambda^2)$ independent of the nature of the diluent. The purpose of the experiments described here is to test the validity of eq 1 and attendant assumptions.

Flory's recent contributions to elasticity theory have evolved to give ever better agreement with experiment,[2,3,8] both for stress–strain isotherms and for the swelling experiments discussed here. The current form of the theory is briefly reviewed, and its relation to experimental results is discussed.

Experimental Section

The PDMS used for this study was kindly supplied by Professor J. E. Mark. The cross-linked sample had been cured in bulk by irradiation with 4.03 Mrd of γ radiation from a ^{60}Co source. Equilibrium swelling in benzene at 30 °C occurred at 0.242 polymer volume fraction, while in cyclohexane at 25 °C it was at 0.156 polymer volume fraction.[9] The un-cross-linked PDMS

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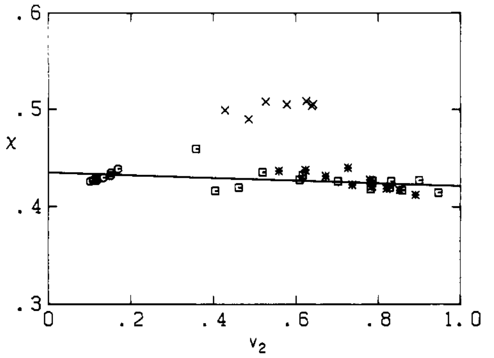

Figure 1. Measured Flory–Huggins interaction parameter χ as a function of the volume fraction v_2 of PDMS in cyclohexane: squares and stars, our vapor sorption data at 30 °C; circles, osmotic data of Kuwahara et al.[11] at 20 °C; crosses, vapor sorption data of Shih and Flory[12] at 25 °C.

and cyclohexane used were described in a previous paper.[1]

Spectrophotometric grade benzene (Mallinckrodt) was used for measurements in the vapor sorption apparatus. The density of benzene at 30 °C is reported[10a] to be 0.8683 g/cm^3, and its vapor pressure[10b] is 119.374 torr.

The vapor sorption apparatus[7] and experimental technique[1] have been previously described.

Results and Discussion

Integral sorption and activity measurements yield the Flory–Huggins interaction parameter, $\chi(v_2)$, as a smoothed function of the un-cross-linked polymer volume fraction, v_2. Results for PDMS + cyclohexane are shown in Figure 1. The solid line is a least-squares fit through our data at high concentrations and Kuwahara's[11] at low concentrations. The equation for the solid line is

$$\chi = 0.435 - 0.014v_2 \tag{2}$$

The representative osmotic results of Kuwahara, Okazawa, and Kaneko[11] at 20 °C that are represented in Figure 1 have not been corrected to 30 °C because the enthalpy of mixing for this system is not large.[1] Our data consist of results from two separate runs using different un-cross-linked PDMS samples from the same lot. There is good agreement between the two data sets.

Shih and Flory[12] have also measured χ for the PDMS + cyclohexane system at 25 °C. Their vapor sorption measurements are also shown in Figure 1; they differ from ours by approximately 18%. The good agreement between our data for separate runs leads us to believe that our results are not in error.

Data for PDMS + benzene at 30 °C are not shown; they are, within experimental error, identical with the results of Shih and Flory[12] at 25 °C. The equation for the least-squares line through our vapor sorption data at high concentration and Shih and Flory's osmotic data at low concentration is

$$\chi = 0.477 + 0.315v_2 \tag{3}$$

For this system, the reduced partial molar residual enthalpy, $\kappa = -T(\partial\chi/\partial T)_{P,v_2}$, ranges from 0.214 at infinite dilution to 0.579 for $v_2 = 0.9$, as determined from eq 46 and 52 of ref 13 using the equation-of-state parameters given by Shih and Flory.[12,14] Thus the enthalpy of mixing for this system is not large, and no temperature correction has been applied to the Shih–Flory osmotic data.

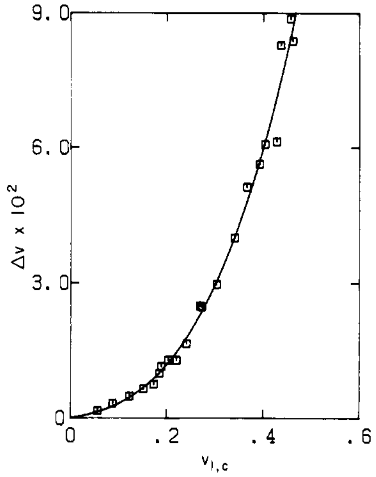

Figure 2. Volume fraction difference vs. volume fraction of cyclohexane in the cross-linked PDMS at 30 °C.

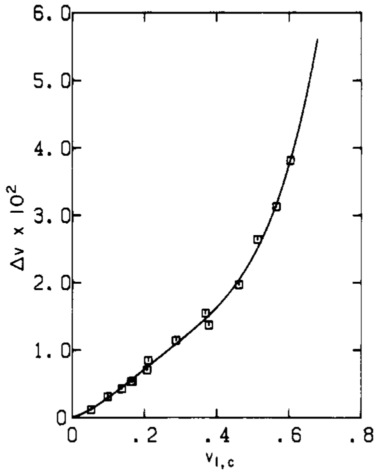

Figure 3. Volume fraction difference vs. volume fraction of benzene in the cross-linked PDMS at 30 °C.

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 polymer. Experimental results for PDMS + cyclohexane are shown in Figure 2. The solid curve in Figure 2 is a fourth-degree, least-squares polynomial which is constrained to pass through the origin; its equation is

$$\Delta v = 0.0156v_{1,c} + 0.1924v_{1,c}^2 - 0.5897v_{1,c}^3 + 0.6660v_{1,c}^4 \tag{4}$$

Experimental results for PDMS + benzene are shown in Figure 3. The solid curve in Figure 3, a similarly constructed and constrained fourth-degree polynomial, is given by

$$\Delta v = 0.0173v_{1,c} + 0.0978v_{1,c}^2 + 0.5394v_{1,c}^3 + 0.1161v_{1,c}^4 \tag{5}$$

Some of the χ data in the high- and low-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. At low polymer concentrations the difference between the activity and unity becomes the important quantity, and chemical potentials are subject to large relative errors. However, the errors in the differential and integral mass measurements remained nearly constant throughout this concentration range.

Activity data are obtained by inserting our smoothed functional representations for $\chi(v_2)$ into the mixing contribution to the solvent chemical potential in the form

$$a_1 = v_{1,u} \exp[v_{2,u} + v_{2,u}^2\chi(v_{2,u})] \tag{6}$$

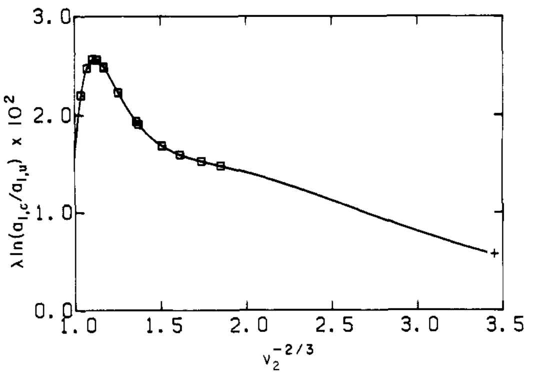

Figure 4. Plot of $\lambda \ln (a_{1,c}/a_{1,u})$ vs. $v_2^{-2/3}$ as a smooth function for PDMS + cyclohexane at 30 °C. The + represents the swelling equilibrium point.[9]

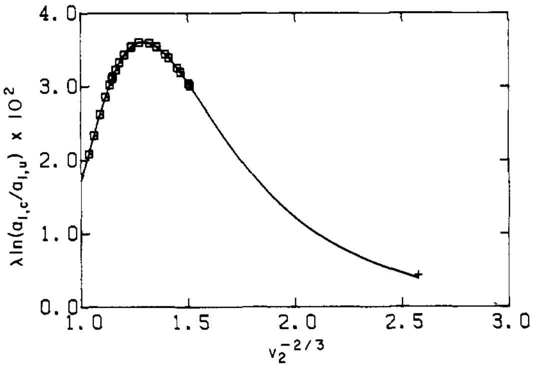

Figure 5. Plot of $\lambda \ln (a_{1,c}/a_{1,u})$ vs. $v_2^{-2/3}$ as a smooth function for PDMS + benzene at 30 °C. The + represents the swelling equilibrium point.

The procedure used to calculate the ratio $a_{1,c}/a_{1,u}$ at equal polymer volume fractions has been previously illustrated.[1]

Derived values of $\lambda \ln (a_{1,c}/a_{1,u})$ have been plotted against $v_2^{-2/3}$ for PDMS + cyclohexane and PDMS + benzene in Figures 4 and 5, respectively. For each the macroscopic deformation is given by $\lambda = v_2^{-1/3}$. The solid lines in Figures 4 and 5 were generated following the above referenced procedure[1] by using values of $v_{1,c}$ ranging from 0.001 to that of swelling equilibrium. The squares in these figures represent the concentrations at which data were collected; their ordinates have been smoothed as described above. The swelling equilibrium points were calculated from

$$\ln (a_{1,u}/a_{1,c}) = \ln (1 - v_{2,s}) + v_{2,s} + \chi v_{2,s}^2 \qquad (7)$$

where $v_{2,s}$ is the volume fraction of cross-linked polymer at swelling equilbrium, and χ is obtained by interpolation using either eq 2 or eq 3, respectively. Swelling equilibrium data were *not* included in the polynomial fits given in eq 4 and 5. As can be seen in Figures 4 and 5, $\lambda \ln (a_{1,c}/a_{1,u})$ exhibits a maximum when plotted against $v_2^{-2/3}$ for both systems. Such maxima have been found in all systems studied to date, both solution and bulk cured. Table I contains a summary of these systems, the locations of their maxima, and the network cure types. A comparison made between the bulk- and solution-cured[1] PDMS + cyclohexane systems reveals that a sharper maximum occurs at a slightly lower dilation (1.12 vs. 1.22) for the bulk-cured sample, but the numerical values of $\lambda \ln (a_{1,c}/a_{1,u})$ for each system are nearly the same. However, there are marked differences between the two bulk-cured PDMS + benzene systems. The maximum for the present sample occurs at a lower dilation (1.27 vs. 1.5) and has a magnitude approximately 3 times greater (3.6 vs. 1.2) than that of Yen and Eichinger.[7] Gross differences between the network structures of the PDMS samples studied might account for this difference. Unfortunately, the equilibrium swelling point for the sample studied by Yen and Eichinger was not determined, thus precluding a comparison on that basis.

Table I
Summary of Differential Swelling Data

system	max location $v_2^{-2/3}$	swelling equil	cure type
NR + benzene[6]	1.8	0.304	bulk
SBR + benzene[7]	1.8		bulk
SBR + *n*-heptane[7]	1.6		bulk
PDMS + benzene[7]	1.5		bulk
PDMS + cyclohexane[1]	1.22	0.159	solution
PDMS + cyclohexane	1.12	0.156	bulk
PDMS + benzene	1.27	0.242	bulk

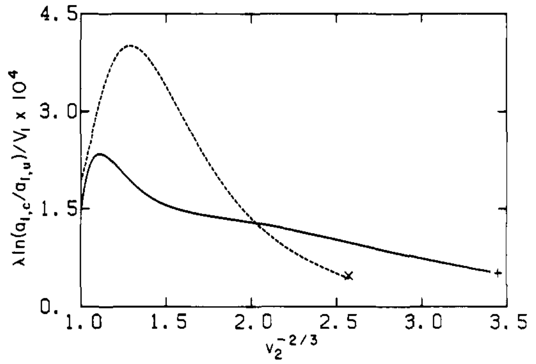

Figure 6. Plot of $\lambda \ln (a_{1,c}/a_{1,u})/V_1$ vs. $v_2^{-2/3}$ for PDMS + cyclohexane (solid line) and benzene (dotted line) systems. The + and × represent the swelling equilibrium points for PDMS + cyclohexane[9] and benzene, respectively. The ordinate has dimensions of mol/cm^3.

In Figure 6 values of $\lambda \ln (a_{1,c}/a_{1,u})$, reduced by the corresponding solvent molar volumes V_1, for the two PDMS + solvent systems are plotted. The ordinates for the swelling equilibrium points are close in value (0.521 and 0.477 for benzene and cyclohexane, respectively) but their abscissas are very different. The same PDMS elastomer was used for both series of measurements. According to theory, the two curves should coalesce, but they do not. Yen and Eichinger[7] have also observed that similarly constructed curves for SBR + benzene and SBR + *n*-heptane failed to coalesce.

The origin of this anomaly, which implies that mixing and elastic free energies are not strictly separable, is an open question at the present time. We might, however, consider a few potential sources of the discrepancy. Throughout the above calculations, it has been assumed that the interaction parameters of the cross-linked and un-cross-linked polymers are equal, for equal polymer volume fractions. Perhaps this is not the case, and the differences in the reduced values of $\lambda \ln (a_{1,c}/a_{1,u})$ are the result of differences between the interaction parameters. If this is the case, an additional term of the form $(\chi_c - \chi_u)/\lambda^5$ should be included in the experimentally measured values of $\lambda \ln (a_{1,c}/a_{1,u})$, where χ_c and χ_u refer to the interaction parameters for the cross-linked and un-cross-linked polymers, respectively. If one designates a reference system (polymer + diluent) for which $\chi_c = \chi_u$ at all volume fractions, the interaction parameter differences can be calculated for another (test) system through comparison of the differences between values of $\lambda \ln (a_{1,c}/a_{1,u})/V_1$ for the reference and test systems at equal polymer volume fractions. The differences for the PDMS + cyclohexane

Table II
Interaction Parameter Difference between Cross-Linked and Un-Cross-Linked PDMS in Cyclohexane

λ^2	$(\chi_c - \chi_u) \times 10^2$	χ_j
1.10	0.94	1.36
1.25	3.67	4.10
1.50	5.54	5.97
1.70	9.19	4.62
1.95	1.04	1.47
2.05	−0.26	0.17
2.15	−1.57	−1.14
2.30	−3.38	−2.95
2.55	−6.16	−5.73

system, choosing PDMS + benzene as the reference system, are shown in Table II. The differences between the interaction parameters do not seem to be large, but in fact they imply large differences between interaction parameters for junctions and chains.

The interaction parameter for a network can be cast in the form[15]

$$\chi_c v_2 = \chi_j v_{2j} + \chi_u v_{2u} \qquad (8)$$

where the subscripts j and u refer to contributions from junctions and chains, respectively. Table II lists values of χ_j for the given interaction parameter differences if the junctions are assumed to comprise 1% of the network volume. (One percent is a conservative estimate for the junction volume fraction of our PDMS network. If phantom network behavior[16] occurs at swelling equilibrium[2,3,17] and the junctions are tetrafunctional, the junction density is approximately 5×10^{-5} mol/cm^3. Taking the volume of a junction as twice that of a solvent molecule yields $v_{2j} = 0.01$.) It will be noted from Table II that χ_j has to have a large magnitude and variable sign to account for the differences between the two systems.

Candau et al.[18] have studied the polymer–solvent interaction parameter of linear, comb-shaped, and star-shaped polystyrenes with high segment densities as a function of solution concentration. They determined that for both good and poor solvents χ is a function of the intramolecular polymer segment density as well as concentration, with the effect of structure being greatest at low polymer concentrations. (The interaction parameter for stars differs from that for linear samples by at most 10% in all the reported systems.[18]) However, this structural influence on χ tends to disappear at greater polystyrene volume fractions ($v_2 > 0.1$). Our experiments were conducted at polymer volume fractions much greater than 0.1 in a concentration region where the intramolecular polymer segment density has very little influence upon the interaction parameter. Noting also that structural influences change χ by at most 10% (stars resemble junctions), the large value and sinusoidal behavior of the calculated χ_j's are beyond what one can reasonably expect for the source of the anomaly.

It could be argued that there is a solvent concentration gradient surrounding the network junctions, resulting in a χ_j which differs from χ_u. If this were the case, the polymer segment density would increase near junctions, increasing the local v_2 such that the structural differences exert an even smaller influence on χ. Thus we believe that the difference between the curves for $\lambda \ln (a_{1,c}/a_{1,u})/V_1$ cannot be explained by asserting that there are significant differences between the cross-linked and un-cross-linked polymer–solvent interaction parameters in the concentration range from pure elastomer to swelling equilibrium.

It is also conceivable that a solvent dependence of the chain dimensions is influencing the swelling behavior. This is a difficult factor to assess because there is not yet a complete theory for the concentration dependence of the dimensions of linear chains. Nevertheless, it seems that such a contribution would be too small to account for the anomaly. The maxima in the swelling functions occur at volume fractions near 0.84 (cyclohexane) and 0.70 (benzene). Surely linear chains are essentially unperturbed in equivalent highly concentrated solutions. Yu and Mark[19] found concentration-dependent chain dimensions from stress–strain isotherms only for more highly swollen PDMS.

Analysis Using Flory Theory

Flory's[2,3] recent elasticity theory has undergone some modifications, and the most recent version will be outlined here. The basic concept in this treatment is that a strained polymer network experiences a transition between two extremes of behavior. At small strains, the entanglement constraints on junctions predominate, and affine behavior is observed. At higher strains and/or at greater dilutions, entanglement constraints become less severe, and phantom network behavior[16] is approached.

Flory's[8] theory now includes the effects of topological irregularities within the network. The equations of ref 2 are to be replaced by

$$\sigma_\lambda^{-1} = \lambda^2 \sigma_1^{-1} + \lambda^3 \sigma_2^{-1} \qquad (9a)$$

$$\sigma_0^{-1} = \sigma_1^{-1} + \sigma_2^{-1} \qquad (9b)$$

with

$$\sigma_1 = 1/2\langle(\Delta x_1)^2\rangle \qquad (9c)$$

$$\sigma_2 = 1/2\langle(\Delta x_2)^2\rangle \qquad (9d)$$

where Δx_1 represents the displacement from the center of action of an entanglement constraint (which deforms affinely) and Δx_2 is an additional displacement introduced by deviations from the perfectly affine state due to structural irregularities. Equation 12 of ref 2 becomes

$$S(\Delta \mathbf{s}) = S_1(\Delta \mathbf{s}_1) * S_2(\Delta \mathbf{s}_2) \qquad (10)$$

where the asterisk denotes the convolution of the two distributions. The equations are developed in a similar manner to those presented previously,[2] with the result

$$\lambda \ln (a_{1,c}/a_{1,u}) = (\xi V_1/V^0)[1 + (\mu_j/\xi)K(\lambda^2)] \qquad (11)$$

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

$$K(\lambda^2) = B[\dot{B}(1 + B)^{-1} + g(\dot{g}B + g\dot{B})(1 + gB)^{-1}] \qquad (12a)$$

$$B = (\lambda - 1)[1 + \lambda - \zeta\lambda^2](1 + g)^{-2} \qquad (12b)$$

$$g = \lambda^2[\kappa + \zeta(\lambda - 1)] \qquad (12c)$$

$$\dot{B} = B[(\lambda - 1)^{-1}(1/2\lambda) + (1 + \lambda - \zeta\lambda^2)^{-1}(1/2\lambda - \zeta) - 2\dot{g}(1 + g)^{-1}] \qquad (12d)$$

$$\dot{g} = \kappa^{-1} - \zeta(1 - 3\lambda/2) \qquad (12e)$$

$$\kappa = \sigma_0/\rho = \langle(\Delta R)^2\rangle/\langle(\Delta x)^2\rangle \qquad (12f)$$

$$\zeta = \rho/\sigma_2 = \langle(\Delta x_2)^2\rangle/\langle(\Delta R)^2\rangle \qquad (12g)$$

The parameters κ and ζ measure, respectively, the severity of constraints exerted by neighboring chains and the severity of fluctuations due to irregularities relative to those of the phantom network. For a perfect tetrafunctional network $\mu_j = \xi$ and $1 + K(\lambda^2)$ becomes proportional to $\lambda\mu_{1,\mathrm{el}}$.

The above formulation is illustrated through calculations shown in Figure 7, where $1 + K(\lambda^2)$ is plotted against $v_2^{-2/3}$ for bulk- and solution-cured polymers. Two general trends

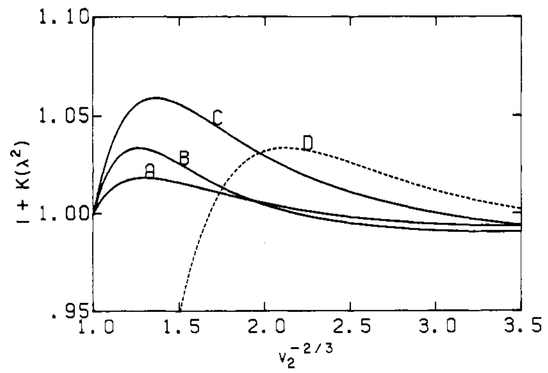

Figure 7. Calculations of $1 + K(\lambda^2)$ vs. $v_2^{-2/3}$ for bulk-cured (solid lines) and solution-cured (dotted line) networks: curve A, $v_2^0 = 1.0$, $\kappa = 3.0$, $\zeta = 0.6$; curve B, $v_2^0 = 1.0$, $\kappa = 10.0$, $\zeta = 0.6$; curve C, $v_2^0 = 1.0$, $\kappa = 10.0$, $\zeta = 0.4$; curve D, $v_2^0 = 0.46$, $\kappa = 10.0$, $\zeta = 0.6$.

are apparent from the bulk-cured curves (curves A, B, and C). First, as κ increases the maximum increases while its location is shifted to slightly lower dilutions, and second, as ζ decreases (κ constant) the maximum becomes more prominent and occurs at higher dilutions. Comparison between solution- and bulk-cured curves (κ and ζ constant) demonstrates that a broader maximum occurs at higher dilutions for the solution-cured case.

Conclusions

This investigation allows comparison of the elastic component of the solvent chemical potential for bulk- and solution-cured PDMS + cyclohexane systems. It reveals that a sharper maximum occurs at a slightly lower dilation for the bulk-cured sample but that numerical values of $\lambda \ln (a_{1,c}/a_{1,u})$ for each system are nearly the same.

The diluent dependence of $\lambda \ln (a_{1,c}/a_{1,u})/V_1$ has been tested. As Figure 6 shows, curves for the PDMS + cyclohexane and PDMS + benzene systems fail to coalesce. This illustrates that $\lambda\mu_{1,\mathrm{el}}/V_1$ is not only a function of dilution, but that there are also specific solvent effects. This anomaly cannot be attributed to differences between χ_c and χ_u or to changes of chain dimensions. This leads us to the inevitable conclusion that the elastic and mixing free energies are not strictly separable.

The newest version of Flory's theory is clearly an improvement over the old. The theory not only shows qualitative agreement with experiment but also is quantitatively more accurate than its predecessor. The experimental maxima occur in the predicted region, and the expected differences between bulk- and solution-cured samples are experimentally confirmed. Hence, apart from the solvent dependence, the theory accounts remarkably well for the swelling behavior of these poly(dimethylsiloxane) samples. Further swelling measurements to test the effect of network topology will be reported.

Acknowledgment. This work was supported in part by Department of Energy Contract DE-AT06-81ER10912. We are indebted to Professor J. E. Mark for a generous donation of samples.

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On the Suppression-of-Junction-Fluctuations Parameter in Flory's Network Theory

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ABSTRACT: The concept of suppression of junction fluctuations in polymer networks is quantified by means of κ in Flory's recent network elasticity theory. The same concept is also measured by the h parameter in Dossin and Graessley's expression for the small-strain modulus. In this work an analytical relationship between these two physically related parameters is obtained for the case of a perfect, incompressible, unswollen network.

A new theory of rubber elasticity has been recently put forward by Flory.[1-3] According to this theory, the fluctuations of network junctions (cross-links) are restricted by the presence of neighboring network strands. The magnitude of constraints depends on network structure, topology, and strain. In a strained phantom network (a model in which network topology is ignored) junction fluctuations give rise to deformation of network strands

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