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Study of Solvent Effects on the Dilation Modulus of Poly(dimethylsiloxane)†

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ABSTRACT: The differential swelling of poly(dimethylsiloxane) (PDMS) model networks, produced by cross-linking silanol-terminated linear PDMS with tetraethoxysilane $Si(OEt)_4$, has been studied to determine the influence of solvent on the observed departures from Flory–Rehner theory. Flory–Huggins interaction parameters and dilation moduli of PDMS with *n*-heptane, 2,3-dimethylpentane (DMP), 2,2,4-trimethylpentane (TMP), and benzene were measured by integral and differential experiments, respectively. It is proven that the dilation modulus has a strong solvent dependence, confirming once again that the Flory–Rehner theory is inadequate. A correlation between the interaction parameter and the dilation modulus is observed; the larger the interaction parameter, the larger is the dilation modulus.

Introduction

Polymer networks have the ability to absorb large amounts of some solvents to become swollen. During swelling, solvent enters the network and mixes with the constituent polymer chains in a process that is driven largely by the entropy increase that attends the formation of any mixture. As the network imbibes solvent, its volume increases, and this forces the polymer chains into less probable, more highly extended, configurations. The chain deformation causes an entropy decrease, but equilibrium can be achieved when these two opposing forces are balanced. This is the essence of the swelling theory of Flory and Rehner.[1] To analyze the problem, Flory and Rehner devised a thermodynamic cycle involving un-cross-linking, swelling, and cross-linking steps that when combined, are equivalent to the original swelling process. They concluded that, during the swelling process, the mixing and the elastic entropies are separable and additive.

We recognize today that generally there will be an enthalpy component in all of these steps and so generalize their theory to state that the free energy of swelling, ΔG, is given by

$$\Delta G = \Delta G_{\mathrm{m}} + \Delta G_{\mathrm{el}} \tag{1}$$

where ΔG_{m} is the free energy of mixing and ΔG_{el} is the elastic free energy.

With the advent of the Flory–Rehner theory, swelling became an important method for characterizing network properties, such as the cross-linking density.[2] That this is possible follows from the observation that a theory of elasticity, which specifies ΔG_{el}, presumably contains network parameters that might be determined from measurements of ΔG or even more simply from measurements on the state of swelling equilibrium where $\Delta G = 0$.

An ambitious project to use Flory–Rehner theory in the determination of the "validity" of elasticity theories was initiated by Gee, Herbert, and Roberts.[3] Instead of finding in favor of one or another of the theories, their results from delicate measurements of the differential swelling of cross-linked and un-cross-linked natural rubber by benzene showed that no theory of elasticity could account for the data, and they were led to question Flory–Rehner theory itself. Further research, conducted in this laboratory by the co-workers[4–6] of one of us, has confirmed the suspicions of Gee, Herbert, and Roberts. Using improved experimental methods, it has been convincingly demonstrated that Flory–Rehner theory is inadequate. The dilation modulus, to be defined, is found to be solvent dependent, contrary to the assertions of the Flory–Rehner theory.

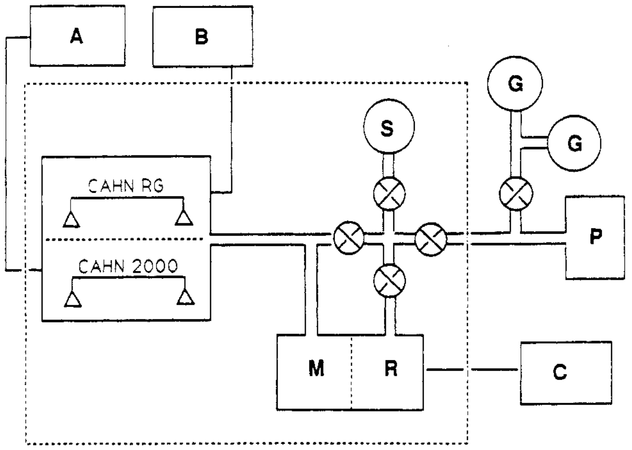

Figure 1. Diagram of the differential swelling instrument. A and B are the control units for the two electronic balances. S is the solvent reservoir. M and R are the measurement and reference sides of the MKS Baratron, and C is the control unit. G represents the pressure gauge (two different thermocouple gauges were used to cover different pressure ranges), and P represents the pumping system. Valves are represented by the symbol (⊗).

The dilation modulus that is measured in the differential swelling experiment is defined as

$$G^{\mathrm{d}} = \frac{\lambda}{V_1} \ln \left(\frac{a_{1\mathrm{c}}}{a_{1\mathrm{u}}} \right) \tag{2}$$

where λ is the extension ratio, $\lambda^3 = V/V_0$, where V_0 is the undeformed volume; V_1 is the molar volume of solvent, and $a_{1\mathrm{c}}$ and $a_{1\mathrm{u}}$ are the solvent activities of cross-linked and un-cross-linked polymers, respectively.

The chemical potentials of a linear polymer solution and a polymer network can be expressed as

$$(\mu_1 - \mu_1{}^{\circ})_{\mathrm{m}} = RT \ln (a_{1\mathrm{u}}) \tag{3}$$

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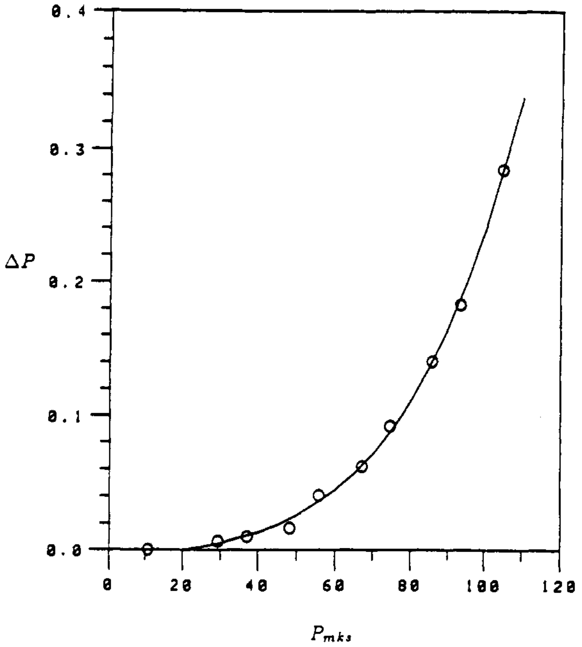

Figure 2. Plot of the pressure gauge calibrated correction ΔP vs P_{MKS}.

and

$$\mu_1 - \mu_1^\circ = RT \ln (a_{1c}) \tag{4}$$

respectively. It follows from the Flory–Rehner assumption that

$$RT \ln (a_{1c}) = RT \ln (a_{1u}) + (\partial \Delta G_{el}/\partial n_1)_{T,P} \tag{5}$$

The dilation modulus is defined as

$$G^d = \frac{1}{3RT\lambda V_0}\left(\frac{\partial \Delta G_{el}}{\partial \lambda}\right)_{T,P} \tag{6}$$

where the elastic free energy ΔG_{el} can be obtained from rubber elasticity theories.

According to Mooney–Rivlin[7,8] phenomenological theory

$$G^d = \frac{2}{RTV_0}(C_1 - C_2/\lambda^4) \tag{7}$$

where C_1 and C_2 are phenomenological elastic constants. The Wall–Flory[9,10] theory gives

$$G^d = \frac{\nu}{V_0}(1 - 1/2\lambda^2) \tag{8}$$

where ν is the number of polymer chains, and James–Guth[11,12] theory gives

$$G^d = \xi/V_0 \tag{9}$$

where ξ is the cycle rank, which is the number of cuts one has to make to reduce a network to a tree. Flory–Erman[13] theory yields the more complicated function

$$G^d = \frac{\xi}{V_0}[1 + (\mu/\xi)K(\lambda)] \tag{10}$$

where μ is the number of junctions and $K(\lambda)$ is a function of λ only.

Although the dilation moduli obtained from the prevalent theories have different forms, they are all independent of solvent and are functions of the properties of the polymer network only. In this paper we will explore whether or not any of these equations is correct, and, if not, our aim is to determine how the solvent influences the dilation modulus.

Experimental Section

1. **Sample Preparation.** Poly(dimethylsiloxane) (PDMS) was selected as the polymer sample because of the ease with which one can make model networks by end-linking reactions. Linear hydroxyl-terminated PDMS, with an average molecular weight 26 000, as determined from bulk viscosity measurements, was purchased from Petrarch Systems, Inc. Before use it was purified under vacuum for 48 h at room temperature.

The whole polymer was fractionated according to the procedure described by Flory.[14] Toluene was used as solvent and acetonitrile as precipitant.[15] The second fraction was retained, coagulated by the precipitant, and dried under vacuum until the weight became constant. The molecular weight was determined viscometrically (Ubbelohde viscometer) to be 41 000 with use of the relationship $[\eta] = 2.00 \times 10^4 M^{0.66}$ for PDMS in toluene at 20 °C as established by Barry.[16]

The polymer was cross-linked with use of electronic-grade tetraethoxysilane $Si(OEt)_4$ (Aldrich; used without further purification). The amount of cross-linker used was that required for complete reaction to form tetrafunctional junctions. Stannous 2-ethylhexanoate at 0.3% by weight was used as catalyst. Since $Si(OEt)_4$ is very sensitive to water, all the ingredients were weighed and mixed in a dry box. Thereafter, the syrup was poured into a Teflon mold and cured under vacuum at room temperature for 48 h. The partially cured sample was turned over after the first 24 h to aid the evaporation of small molecules.

Sol extraction[15] was performed by first swelling the network in tetrahydrofuran for 3 days and then in toluene for another 3 days. Thereafter the sample was deswollen in a series of toluene–methanol mixtures of increasing methanol content and finally in pure ethanol. The ethanol was evaporated under vacuum at room temperature for 2 days until a constant weight was obtained. The sol fraction, defined as the ratio of the weight differences before and after sol extraction to the original weight, was 1.9%, and the gel fraction was therefore 98.1%.

Benzene, *n*-heptane, 2,3-dimethylpentane, and 2,2,4-trimethylpentane were chosen as solvents for the vapor sorption studies. All were purchased from Aldrich, and they were purified by the freeze–pump–thaw method.

2. **Instruments and Calibration.** The differential swelling instrument consists of two electronic balances: a Cahn RG and a Cahn 2000. The electronic balances are assembled inside a stainless steel chamber which is connected to a solvent reservoir, an MKS capacitance diaphragm-type pressure gauge, and the vacuum line (see Figure 1). The various components of the system can be isolated from one another by use of control valves. During measurements, the balance chamber, solvent reservoir, and gas manifold are submerged in a water bath (Tronac, Inc.). The MKS sensor head is located in a submarine submerged in the same bath and, when required (to prevent condensation of vapor in the sensor head feed lines), is maintained at a temperature a few degrees warmer than the surrounding bath. For these studies, the temperature of the entire system was controlled at 30.00 ± 0.05 °C.

The MKS pressure gauge was calibrated with a Ruska 2465 gas-lubricated dead weight piston pressure gauge. The difference between the actual pressure and the MKS pressure gauge reading, $\Delta P = P - P_{\mathrm{MKS}}$, is plotted against P_{MKS} in Figure 2. The data were fitted to a fourth-degree polynomial[17] to obtain

$$\Delta P = -3.4361 \times 10^{-4} P_{\mathrm{MKS}} + 2.1065 \times 10^{-5} P_{\mathrm{MKS}}^2 - 2.1534 \times 10^{-7} P_{\mathrm{MKS}}^3 + 2.7801 \times 10^{-9} P_{\mathrm{MKS}}^4 \tag{11}$$

This result was applied in the data analysis to correct the MKS gauge pressure readings.

The Cahn RG balance was used to directly measure the differential sorption of solvents between two samples. One (the un-cross-linked polymer) was placed on the sample pan, and the other (the cross-linked polymer) was placed on the reference pan. During the experiment, the weight of the sample on the reference side changes, and this necessitates a further calibration of the arm length ratio of the balance beam. This was done using the procedure described previously.[6] The arm length ratio, *r*, was found to be 0.9861, and the balance constant, *C*, was concurrently determined to be 0.9999. All electronic balances

Table I
Physical Properties of PDMS and Solvents[a] at 30 °C

substance	density (g cm^{-3})	$P_1°$ (Torr)
PDMS	0.9653[19]	
benzene	0.8685	119.34
n-heptane	0.6753	58.38
2,3-dimethylpentane	0.6865	86.62
2,2,4-trimethylpentane	0.6836	62.41

[a] All data from ref 18 except as noted for PDMS.

were otherwise calibrated following the manufacturer's recommended procedures.

3. Differential Swelling Experiments. Two un-cross-linked PDMS samples were weighed on a Cahn 27 electronic balance. One sample was placed on the pan of the Cahn 2000 to measure the integral weight changes, and the other was placed on the sample pan of the Cahn RG. The cross-linked PDMS sample was also weighed on the Cahn 27 and was then placed on the reference pan of the Cahn RG so that the differential sorption of solvent between the cross-linked and un-cross-linked samples could be measured. The system was then pumped down until the vacuum reached 10^{-4} Torr or the pressure increase of the system was less than 10 mTorr in 48 h after the system was isolated from the pump at the experimental temperature, 30 °C. (Because the entire system is fairly small, its internal surfaces are not polished. Rough stainless steel takes a long time to degas, and we were unable to bake the system because to do so would have damaged the balances. The pressure increase that was observed in the isolated system was judged to be caused entirely by outgassing. Experience demonstrated that a true leak in the system caused a much more rapid pressure rise.) When the desired vacuum was reached the water bath was raised to immerse the system (the dashed part in Figure 1) in water.

After the temperature stabilized, a small amount of solvent vapor was cautiously released from the solvent reservoir and the system was allowed to equilibrate. Usually, 2–24 h was required for the polymer samples to absorb their equilibrium quantities of solvent. Readings from the MKS display unit and the balance recorders were taken once the readings from all the instruments became sensibly constant. Additional points on the sorption isotherms were collected upon addition of further aliquots of vapor. The system was pumped down periodically to ensure that leak-free conditions were maintained, and reproducibility and reversibility were routinely checked.

4. Data Reduction. The data collected from the experiments are P_1, the pressure of the solvent vapor at equilibrium, m'_{1u}, the mass of the solvent absorbed by the un-cross-linked polymer on the integral sorption balance (Cahn 2000), and $\Delta m_1 = m_{1u} - m_{1c}$ (the difference between the masses of solvent absorbed by the un-cross-linked polymer, m_{1u}, and cross-linked polymer, m_{1c}), on the Cahn RG balance used for the differential measurements. Subscripts 1 and 2 represent solvent and polymer, respectively, and subscripts u and c denote un-cross-linked and cross-linked polymers, respectively.

The volume fraction of solvent in the un-cross-linked polymer ϕ_{1u} is calculated from

$$\phi_{1u} = \frac{m'_{1u}/\rho_1}{m'_{1u}/\rho_1 + m'_{2u}/\rho_2} \tag{12}$$

where m'_{2u} is the dry mass of the polymer on the integral sorption balance, and ρ_1 and ρ_2 are the densities of solvent and polymer, respectively, as given in Table I. The corrected mass of the solvent absorbed by the cross-linked polymer is determined by

$$m_{1c} = (m_{1u} - C\Delta m_1)/r \tag{13}$$

with

$$m_{1u} = \frac{m_{2u}}{m'_{2u}} m'_{1u} \tag{14}$$

where C and r are the balance constant and arm length ratio discussed in the Instruments and Calibration section. The mass of solvent, m_{1u}, is absorbed by the un-cross-linked sample with dry mass m_{2u} on the differential sorption balance. Similarly, the volume fraction of solvent absorbed by the cross-linked sample with dry mass m_{2c} is

$$\phi_{1c} = \frac{m_{1c}/\rho_1}{m_{1c}/\rho_1 + m_{2c}/\rho_2} \tag{15}$$

The volume fraction different $\Delta\phi_1$ is defined as

$$\Delta\phi_1 = \phi_{1u} - \phi_{1c} \tag{16}$$

The raw data from the experiment were smoothed by fitting $\Delta\phi_1$ vs ϕ_{1c} to a fourth-degree polynomial using a fitting routine,[19] but the first five of these data points were first fitted by linear least squares to obtain an intercept (generally very small, but not negligible) that was subsequently subtracted from the values of the ordinates so as to correct $\Delta\phi_1$ to ensure that $\Delta\phi_1$ goes through the origin. Failure to perform this simple correction results in differential sorption isotherms that diverge very strongly at small dilations. In all cases, the corrections that were applied were well within the experimental uncertainties.

Since all experiments were conducted at low pressure (less than 100 Torr) and low temperatures, the solvent vapors can be treated as ideal gases in *all* states, and the activities are therefore simply calculated as

$$a_1 = P/P° \tag{17}$$

where $P°$ is the saturation vapor pressure of the solvent at the experimental temperature, as listed in Table I. Since $\mu_1 - \mu_1° = RT \ln a_1$, it follows from the Flory–Huggins[20,21] theory that the interaction parameter, χ, is given by

$$\chi = \frac{\ln (a_1/\phi_1) - \phi_2}{\phi_2^2} \tag{18}$$

Since the molecular weight of the cross-linked polymer is infinite and that for the un-cross-linked polymer is large, the usual factor $(1 - 1/r)$ that multiplies the ϕ_2 term in eq 18 is set to unity.

The data analysis procedure will be somewhat clearer if we illustrate it with an example. Assume for the moment the validity of eq 9 for the dilation modulus. The combination of eqs 5 and 9 gives

$$\ln (a_{1c}) = \ln (a_{1u}) + \frac{\xi V_1}{V_0\lambda} \tag{19}$$

When the Flory–Huggins expression for a_{1u} from eq 18 is substituted into this equation, one obtains

$$a_{1c} = (1 - \phi_2) \exp(\phi_2 + \chi\phi_2^{\,2} + A\phi_2^{\,1/3}) \tag{20}$$

for the activity of solvent in equilibrium with the swollen network. In eq 20 we have set $A = \xi V_1/V_0$, and use has been made of $\lambda^3 = 1/\phi_2$. This gives us a definite relation that can be discussed quantitatively in comparison with the Flory–Huggins theory.

Plots of a_1 vs ϕ_2 for the un-cross-linked polymer (u) and cross-linked polymer (c) are provided in Figure 3. For both systems we have used the arbitrary, but representative, values $\chi = 0.5$ and $A = {}^1/_{15}$ ($A = 0.0$ for the un-cross-linked system). Note that the complete isotherm are given in Figure 3a, and a blowup is contained in Figure 3b. The point of "swelling equilibrium" obtains when the solvent activity is unity, which for these particular parameters occurs near $\phi_{2c} = 0.48$. It is also of interest to note that the magnitude of the elastic term is quite small compared with the mixing terms. A very delicate experiment is required to determine the elastic contribution to the solvent activity with sufficient accuracy to probe the solvent dependence that is being discussed here.

The differential swelling experiment provides the volume fractions ϕ_{2u} and ϕ_{2c} at a given solvent activity a_1, which correspond to points a and c in Figure 3b, respectively. It follows from eq 18 and this condition that

$$a_{1c}(\text{at point c}) = a_{1u}(\text{at point a}) = (1 - \phi_{2u}) \exp(\phi_{2u} + \chi_u\phi_{2u}^{\,2}) \tag{21}$$

The quantity χ_u will be defined momentarily. To calculate the dilation modulus, we need to know the activities of cross-linked and un-cross-linked polymers at the same volume fraction. The

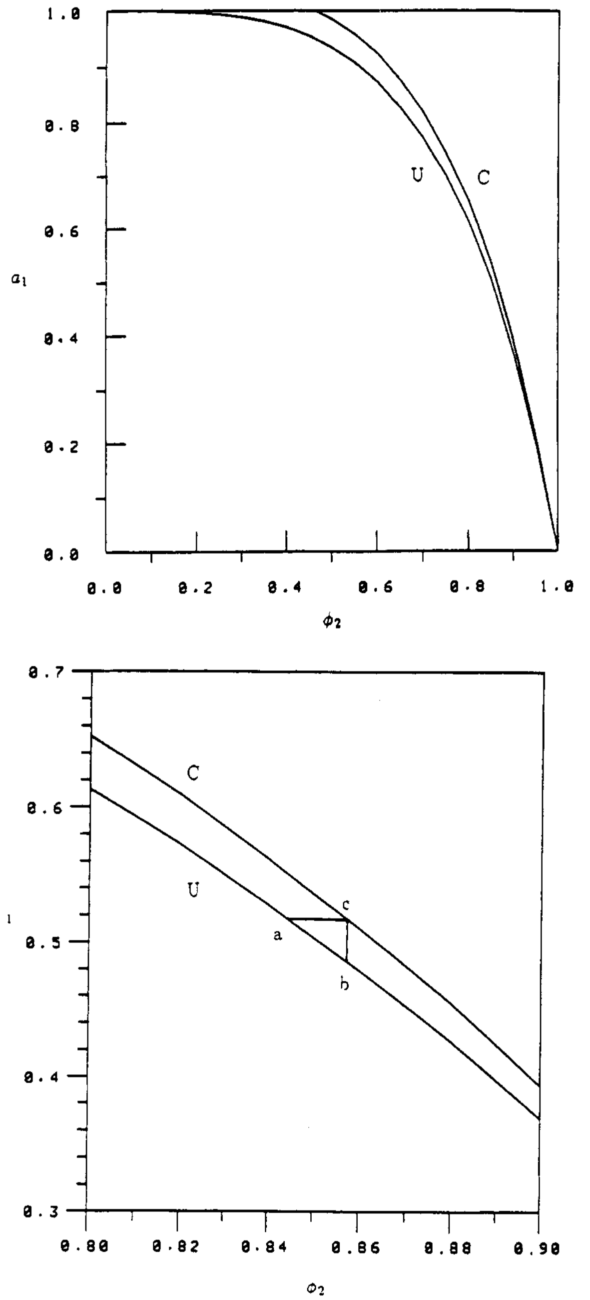

Figure 3. Plots of the hypothetical solvent activities a_1 vs ϕ_2. Part a shows complete curves, and part b is an expanded region of part a. See text for details of the calculation. The symbol C represents the cross-linked polymer, and U represents the un-cross-linked polymer.

quantities a_{1c} (at point c) and ϕ_{2c} are known directly from the experiment, but we need to know a_{1u} (at point b) with $\phi'_{2u} = \phi_{2c}$, which can be easily obtained once we know the value of χ at ϕ_{2c}. This in turn is obtained by smoothing the integral sorption data to obtain χ as a function of composition ϕ_2. This is the meaning of χ_u above; it is the value of χ evaluated at $\phi_2 = \phi_{2u}$. (At this point the illustrative example has been generalized to allow for a concentration dependence of χ, but note that χ as we use it refers *only* to the isotherm for the un-cross-linked system. The total difference between the two curves in Figure 3 is contained in the elastic term alone.) It follows that

$$a_{1u}(\text{at point b}) = (1 - \phi_{2c}) \exp(\phi_{2c} + \chi_c \phi_{2c}^{\ 2}) \qquad (22)$$

Hence, the dilation modulus is readily calculated by combining eqs 21 and 22.

Results and Discussion

Flory–Huggins interaction parameters at 30 °C were obtained from the integral sorption data with use of eq 18.

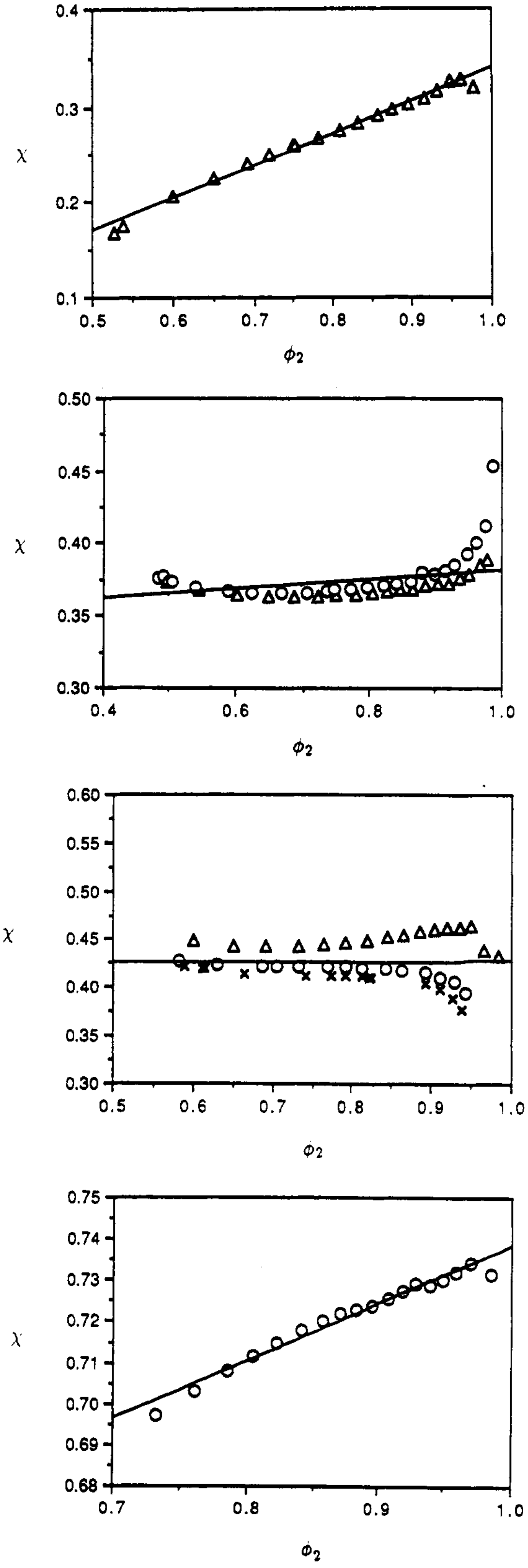

Figure 4. Interaction parameters χ vs ϕ_1 for the following: (a) PDMS + TMP at 30 °C, with triangles representing the experimental data and the solid line being the least-squares fit of the data; (b) PDMS + DMP at 30 °C, where the different symbols represent data from different runs and the solid line is the least-squares fit of the data; (c) PDMS + *n*-heptane at 30 °C, and the different symbols are again data from different runs and the solid line is the least-squares fit; (d) PDMS + benzene at 30 °C, with triangles representing experimental data and the solid line the least-squares fit.

The concentration dependences of the interaction parameters were adequately represented by linear functions of the volume fractions of polymer for all four diluents.

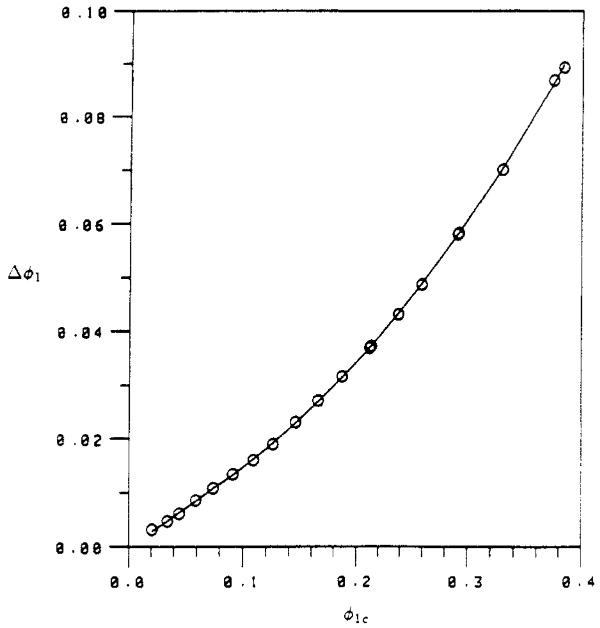

Figure 5. $\Delta\phi_1$ vs ϕ_{1c} for PDMS + TMP at 30 °C. Circles represent experimental data, and the solid line represents the fourth-degree polynomial fit.

Table II
Polynomial Coefficients for $\Delta\phi_1$ vs ϕ_{1c}

	coefficient			
diluent	A_1	A_2	A_3	A_4
n-heptane	0.1495	0.5233	-1.1283	3.3044
2,3-DMP	0.1914	-0.4025	3.2090	-3.6694
2,2,4-TMP	0.1348	0.0677	0.6139	-0.3021
benzene	0.2562	-0.3614	3.5333	4.2258

The slopes and intercepts of the linear equations were obtained through a linear least-squares fit. These results are plotted in parts a–d of Figure 4; the fitted equations for the different systems are as follows:

1. PDMS + 2,2,4-trimethylpentane (TMP),

$$\chi = 0.000 + 0.341\phi_2 \quad (23a)$$

2. PDMS + 2,3-dimethylpentane (DMP),

$$\chi = 0.349 + 0.033\phi_2 \quad (23b)$$

3. PDMS + *n*-heptane, $\chi = 0.423 + 0.004\phi_2$ (23c)

4. PDMS + benzene, $\chi = 0.599 + 0.139\phi_2$ (23d)

The values of the intercepts at $\phi_2 = 0$ should be interpreted cautiously; it is a long extrapolation from the range over which the data were taken to $\phi_2 = 0$. The precision of the results contained in eq 23a–d was established by standard propagation of error methods.[22]

The interaction parameters measured for benzene at 30 °C are in agreement with the results of Brotzman[5] and Neuburger.[6] Summers, Tewari, and Schreiber[23] measured the interaction parameters of *n*-heptane, 2,2,4-trimethylpentane, and benzene by means of gas–liquid chromatography at 25, 40, 55, and 70 °C, and their data are some 10–30% higher than our results. Osmotic pressure measurements[24] of PDMS + *n*-heptane solutions yielded χ values ranging from 0.407 to 0.415 at low polymer concentrations at 35 °C, and our extrapolated value for this solvent agrees remarkably well with the more direct measurements. Activity data for PDMS with 2,3-dimethylpentane have not been reported previously, to our knowledge.

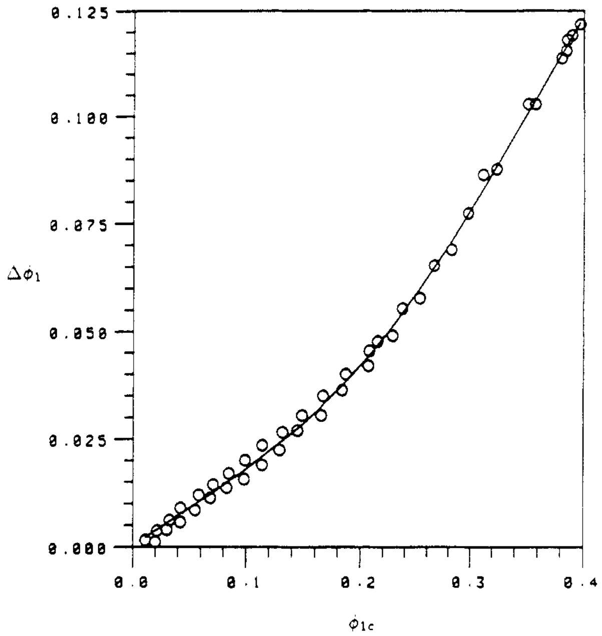

Figure 6. $\Delta\phi_1$ vs ϕ_{1c} for PDMS + DMP at 30 °C. Symbols and curve as in Figure 5.

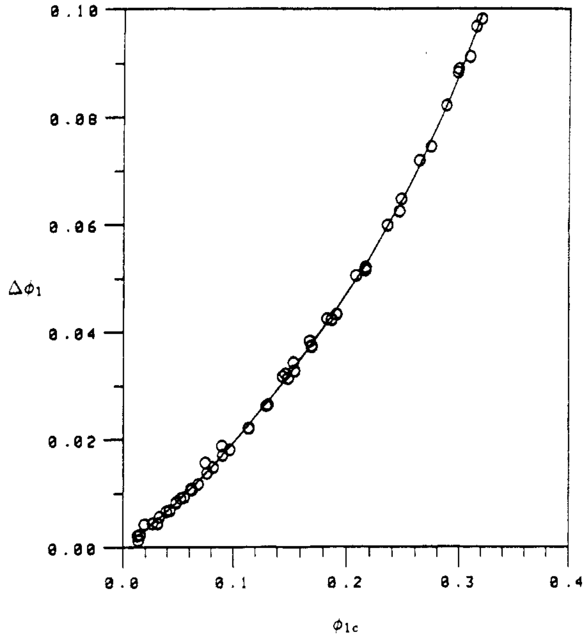

Figure 7. $\Delta\phi_1$ vs ϕ_{1c} for PDMS + *n*-heptane at 30 °C. Symbols and curve as in Figure 5.

To obtain the dilation modulus, the raw data were smoothed by fitting $\Delta\phi_1$ to a fourth-degree polynomial in ϕ_1, as explained in the Data Reduction section. Plots of raw data and the smoothing polynomials are given in Figures 5–8. The coefficients of the fitted polynomials

$$\Delta\phi_1 = \sum_{k=1}^{4} A_k \phi_1^{\,k} \quad (24)$$

are listed in Table II.

The dilation moduli are plotted against λ^2 in Figures 9–12 for the four different systems. For a better visualization of the magnitude of the nonadditivity effect, these values are plotted together in Figure 13. The dilation modulus of PDMS + benzene has the largest magnitude, and our values are in good agreement with those of Neuburger and Eichinger.[6] Values for PDMS + *n*-heptane and PDMS + 2,3-dimethylpentane are comparable and fall between the benzene data and that for PDMS + 2,2,4-

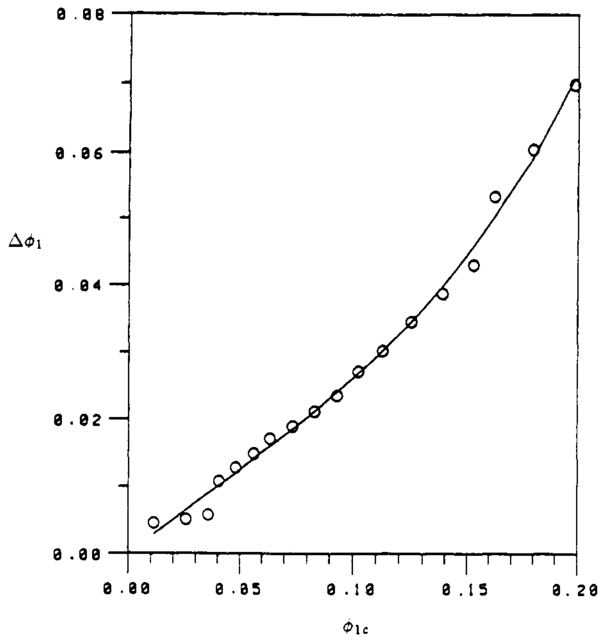

Figure 8. $\Delta\phi_1$ vs ϕ_{1c} for PDMS + benzene at 30 °C. Symbols and curve as in Figure 5.

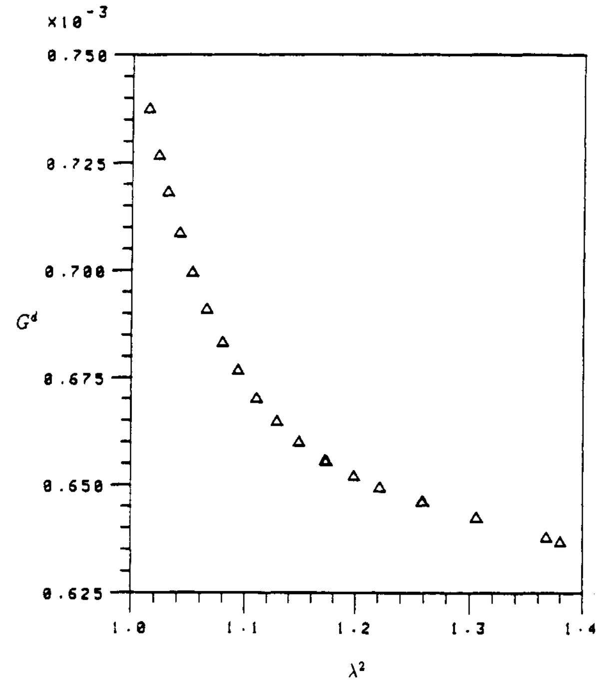

Figure 9. Dilation modulus G^d vs λ^2 for PDMS + TMP.

trimethylpentane, which has the lowest values of the dilation modulus of all the systems tested. Upon examining the solvent interaction parameters it will be seen that the smaller is the interaction parameter, the smaller is the dilation modulus for that solvent.

The shapes of the dilation moduli vs λ^2 should be interpreted cautiously in the realm of small λ, since the experimental data are subject to large errors at small extension ratios ($\lambda < 1.04$) or, equivalently, high polymer concentrations ($\phi_2 > 0.94$). The values of the dilation moduli derived from the small $\Delta\phi_1$ data points are very sensitive to the method of data analysis.

Some of the data plotted in Figure 13 are replotted in Figure 14 along with several theoretical predictions (see the above theories of elasticity), all based on the assumed validity of the Flory–Rehner theory. The solid curve represents the prediction from eq 7 with $2C_1/RTV_0 = 0.0013$ and $2C_2/RTV_0 = 0.000\,65$, while the long-dashed

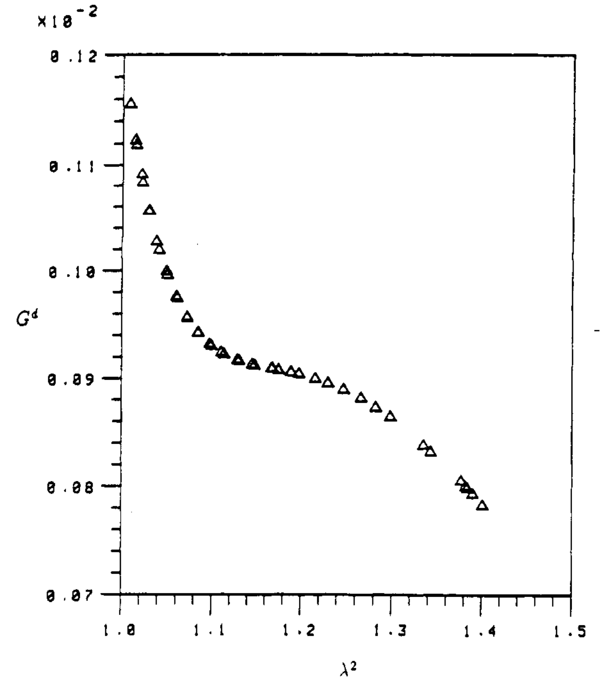

Figure 10. Dilation modulus G^d vs λ^2 for PDMS + DMP.

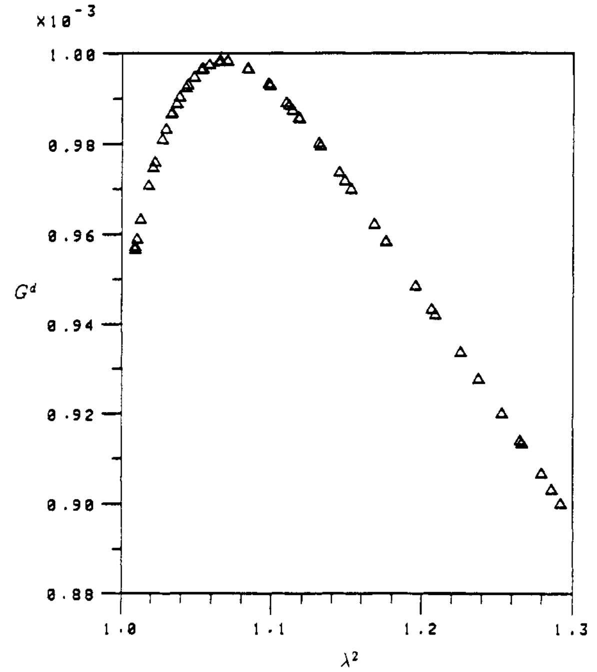

Figure 11. Dilation modulus G^d vs λ^2 for PDMS + *n*-heptane.

curve results from eq 8 with $\nu/V_0 = 0.0013$. The dotted line is the James–Guth result (eq 9), while the short-dashed curve is that of Flory–Erman theory (eq 10). For calculations with the latter theory, the value of ξ/V_0 was chosen to be half of the value of ν/V_0, 0.000 65, used for the Wall–Flory example. This value was chosen so as to satisfy the relationship between ξ and ν for a perfect tetrafunctional network.[25] The κ parameter in the Flory–Erman theory is a measure of the severity of the constraints imposed on the junctions by neighboring chains relative to those imposed by a network of phantom chains,[25] and its value was chosen to be 4.5. To be sure, the theoretical values of the dilation moduli depend on the choices made for the parameters in eqs 7–10, and other choices might improve the quality of the fits. However, that is a futile exercise because none of the theories has the correct functional form to account for the experimental results, and because all must be applied within the context of the Flory–Rehner

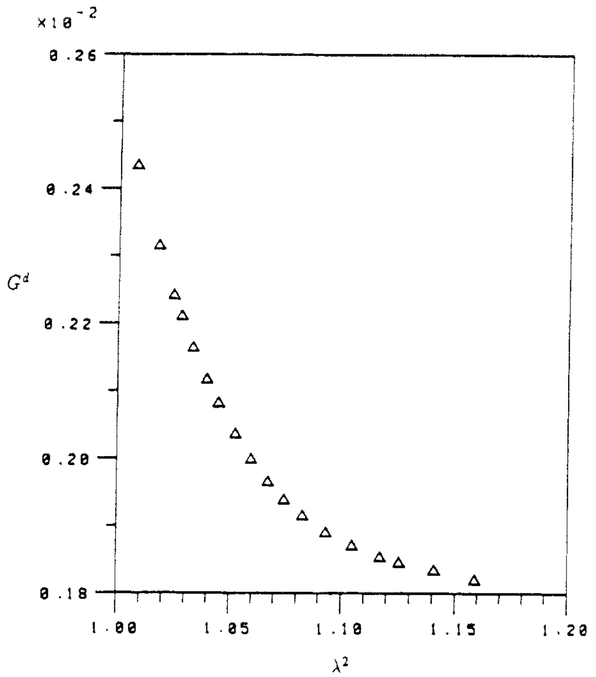

Figure 12. Dilation modulus G^d vs λ^2 for PDMS + benzene.

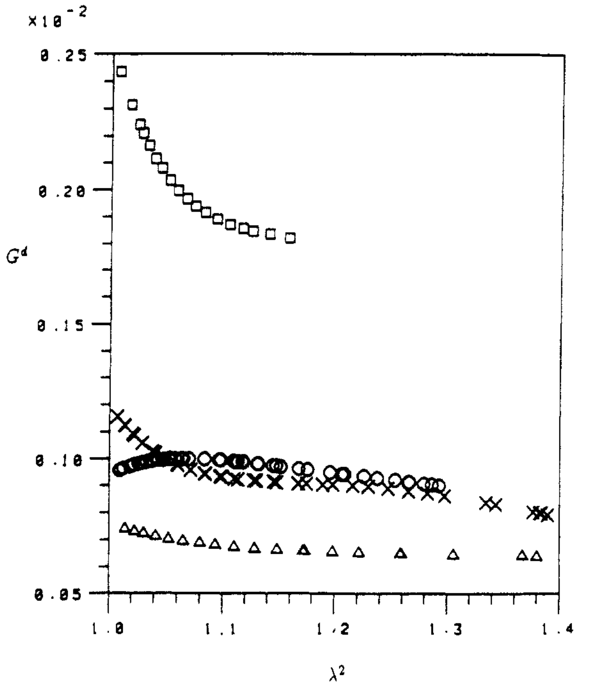

Figure 13. Combined data from Figures 9–12 for PDMS with respectively benzene (squares), *n*-heptane (circles), DMP (crosses), and TMP (triangles).

theory, all are mute on the subject of the observed solvent dependence. None of the theories of elasticity reviewed here can account for the data; Flory–Rehner theory does not hold, and none of them predicts the correct functional dependence of the dilation modulus on extension ratio.

Conclusions

It may be of interest to point out that the pattern of the data presented here is consistent with that observed for the temperature dependence of dilation moduli. In previous work in this series, it was reported[6] that the dilation moduli of two PDMS networks with benzene and cyclohexane at 20 °C are larger than those at 30 °C. The observed temperature coefficients of the dilation moduli are too large to be explained by the temperature dependence of either $\langle r^2\rangle_0$ or V_0.[26] However, these systems are endothermic, and the interaction parameters at 20 °C are larger than those at 30 °C. The differences in dilation moduli at different temperatures thus may be attributed to the differences in the interaction parameters, consistent with the variations seen here. The opposite sign should be observed for exothermic systems, and it would be interesting to test this hypothesis.

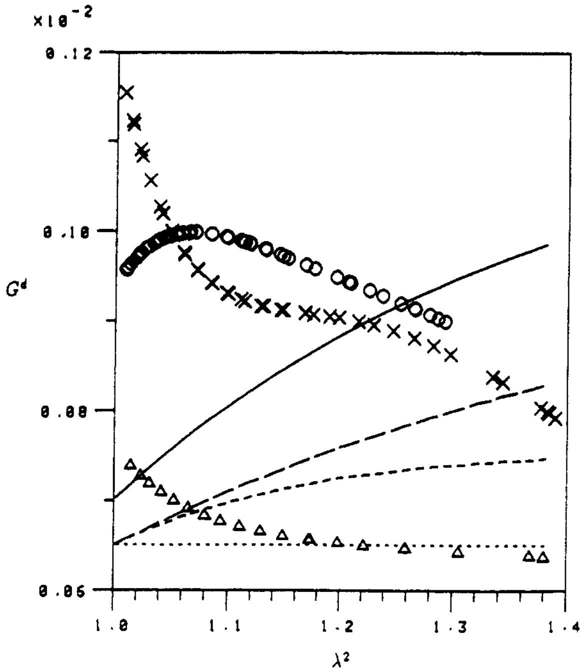

Figure 14. Comparison of experimental results and theoretical predictions. The dilation modulus G^d from the Mooney–Rivlin equation with $2C_1/RTV_0 = 0.0013$ and $2C_2/RTV_0 = 0.000\,65$ is represented by the solid line, and that from Wall–Flory theory with $\nu/V_0 = 0.0013$ is given by the long-dashed line. Results from James–Guth and Flory–Erman theories are represented by the dotted line and the short-dashed line, respectively, with $\xi/V_0 = 0.000\,65$ applying to both and with $\kappa = 4.5$ (see text and ref 13) for the latter.

We have not completely ruled out the possibility that specific solvent effects on chain dimensions might also contribute to the trends that are seen in the data. However, we think that this explanation is extremely unlikely for the highly concentrated systems that are studied in swelling experiments; they are way above the overlap concentration.

We believe that Flory–Rehner theory is disproved, and the challenge now is to develop a comprehensive theory of elasticity that is consistent with these results. The accompanying paper shows that a new rubber elasticity theory developed by one of us[27] can be applied to the swelling process and it is a positive step in accounting for the solvent dependence of the dilation modulus that has been demonstrated here. The earlier results of Yu and Mark[28] showing a specific solvent effect on the modulus of elasticity might also be explained in this context.

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Registry No. DMP, 565-59-3; TMP, 540-84-1; heptane, 142-82-5; benzene, 71-43-2.