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Critical Experimental Test of the Flory–Rehner Theory of Swelling

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ABSTRACT: Differential swelling measurements performed on two poly(dimethylsiloxane) (PDMS) networks are reported. The two elastomers are closely similar to one another except for the chemical structures of the cross-links, which are quite different. The samples were swollen in benzene and in cyclohexane at 20 °C and at 30 °C. The reduced dilation moduli of the two samples parallel one another in a given solvent at a fixed temperature, but they reveal solvent and temperature dependences that are not encompassed by any known theory. The results demonstrate conclusively that the assumption of separability of mixing and elastic free energies is incorrect and that the Flory–Rehner theory of swelling is in need of modification.

Introduction

For the past 40 years, the phenomenon of swelling has been used to analyze the physical properties of elastomers. The criterion for swelling equilibrium was first recognized by Frenkel[1,2] and was later developed by Flory and Rehner[3,4] into a general theory. Flory–Rehner theory is based on two peculiar properties of elastomers, which distinguishes them from other typical solids: They absorb large amounts of solvent without dissolving, and they undergo large deformations with correspondingly small stresses. The major hypothesis of Flory and Rehner is that the free energy change on swelling an elastomer consists of two contributions, which they assumed to be separable and additive. These are the free energy of mixing, ΔG_{m}, and the free energy of elastic deformation, ΔG_{el}. Thus, the free energy change accompanying the absorption of a diluent was assumed to be given by

$$\Delta G = \Delta G_{\mathrm{m}} + \Delta G_{\mathrm{el}} \qquad (1)$$

The general theories of mixing and of rubber elasticity are well-known. Polymer solution theory was developed independently by Flory[5] and Huggins.[6-8] They calculated the enthalpy of mixing by counting the number of polymer–solvent contacts, and the entropy of mixing by counting the number of different configurations possible for the polymer–solvent system. There are several theories of elasticity, the most familiar of these being due to Wall and Flory[9-13] and to James and Guth.[14-19] Both of these theories treat the elastomer as an assembly of randomly coiled chains linked together into a coherent network by chemical bonds.

The virtue of swelling is that it is a relatively simple method for characterizing elastomers. According to eq 1 and depending on the applicable theory of ΔG_{el}, measurements conducted at swelling equilibrium will directly yield the modulus of elasticity. With somewhat more effort than that needed for swelling equilibrium measurements, the solvent activity can be varied so as to swell the elastomer to different extents. This allows one to probe the elastic energy function in domains of deformation not readily accessible in ordinary stress–strain measurements. In view of these facts, elastomer swelling deserves careful consideration, both as a characterization technique and as a basis to test elasticity theory.

Vapor sorption techniques enable one to vary the solvent activity, as was shown in the seminal work of Gee, Herbert, and Roberts.[20] They conducted experiments that allowed them to control the vapor pressure of the solvent, and the amount of the solvent that the polymer absorbed was determined by using a sensitive microbalance housed in a vacuum system. Similar experiments were later conducted by Yen and Eichinger[21,22] using an improved experimental apparatus. Later still, Brotzman and Eichinger[23-25] conducted experiments on siloxane networks using the same apparatus. The primary purpose of each of these studies was to probe the elastic theories. However, what they all found was an elastic free energy function that could not be explained with any of the current theories. Even more disconcerting, both Yen and Brotzman found the elastic free energy function to be solvent dependent, thus calling to question the basic assumptions inherent in eq 1. This fact, and the fact that the elastic free energy function shows anomalous behavior, has led to the opinion that the major premise of the theory of swelling of networks, namely, the hypothesis that the elastic and mixing free energies are separable, is questionable.

At the present time, the status of the Flory–Rehner theory is still unresolved. From the experiments recounted above it appears that the theory is in need of modification. There is at least one possibility for the breakdown of the theory, as was first noted by Gee et al.[20] It is possible that the interaction of the solvent with the cross-links is different from that with the midchain segments. If this is the case, the elastic modulus could appear to be solvent dependent because inappropriate account had been taken of the cross-link–solvent mixing term. Calculations[24] to estimate the magnitude of the cross-link–solvent interaction on the swelling measurements showed that this is an unlikely source of the apparent breakdown of the Flory–Rehner theory. To settle this experimentally, we have conducted swelling measurements on two closely similar model networks that have cross-links with quite different structures. If a cross-link–solvent mixing term is important, this experiment should discover it.

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Thermodynamics and Data Analysis

For a cross-linked elastomer that exhibits a high degree of elasticity, Flory and Rehner[3] proposed that the free energy of swelling is given by eq 1. Taking the derivative with respect to the number of moles of the solvent, n_1, at constant temperature and pressure, gives

$$\mu_1 - \mu_1^0 = (\mu_1 - \mu_1^0)_m + \mu_{1,el} \tag{2}$$

The chemical potentials are determined directly from the activities according to the standard relations

$$\mu_1 - \mu_1^0 = (\mu_1 - \mu_1^0)_m + \mu_{1,el} = RT \ln (a_{1,c}) \tag{3}$$

$$(\mu_1 - \mu_1^0)_m = RT \ln (a_{1,u}) \tag{4}$$

where $a_{1,c}$ and $a_{1,u}$ are the activities of solvent for the cross-linked and uncross-linked samples, respectively. The activities are related to the measured pressure, P, and temperature, T, by the relation

$$a_1 = \frac{P}{P^0} \exp\left[\frac{B_2(P - P^0)}{RT}\right] \tag{5}$$

where P^0 is the equilibrium vapor pressure and B_2 is the second virial coefficient of the vapor. Since the second virial coefficients for the solvents used here, benzene and cyclohexane, are small,[26] eq 5 reduces to

$$a_1 = P/P^0 \tag{6}$$

The volume fractions are determined from the masses m_i and densities ρ_i of the components in the binary mixture by means of the equation

$$\Phi_1 = \frac{m_1/\rho_1}{m_1/\rho_1 + m_2/\rho_2} = 1 - \Phi_2 \tag{7}$$

When the cross-linked and uncross-linked samples contain the same concentration of diluent, the difference between eq 3 and 4 yields the elastic contribution to the solvent chemical potential as

$$\mu_{1,el} = RT \ln (a_{1,c}/a_{1,u}) \tag{8}$$

Theoretical elastic free energy functions are generally written in terms of the principle extension ratios λ_i. In a swelling experiment the deformation of the sample is assumed to be isotropic; i.e., $\lambda = \lambda_1 = \lambda_2 = \lambda_3$. The contribution to the solvent chemical potential arising from the elastic response of the network is thus

$$\mu_{1,el} = \left(\frac{\partial \Delta G_{el}}{\partial \lambda}\right)_{T,P} \left(\frac{\partial \lambda}{\partial n_1}\right)_{T,P} \tag{9}$$

The deformation λ is related to the volume by $\lambda^3 = V/V^0$, and if there is no appreciable volume change on mixing, this is in turn given by

$$\lambda^3 = \frac{V}{V^0} = \frac{1}{\Phi_2} \tag{10}$$

It follows that

$$\frac{\partial \lambda}{\partial n_1} = \frac{V_1}{3V^0\lambda^2} \tag{11}$$

where V^0 is the volume of the unswollen sample, V_1 is the molar volume of solvent, and V is the volume of the swollen network. [Strictly speaking, V_1 is the apparent molar volume of the solvent. If the volume change is small, V_1 is safely taken to be the molar volume. The volume changes on mixing for the uncross-linked systems of interest are doubtless small. Our results are not vitiated if the volume change on mixing of PDMS networks with the two solvents considered here are different; it is the magnitude of V_1 that is important to the data analysis, and not the volume change on mixing (which is a minor correction at most).]

The mixing chemical potential for a cross-linked elastomer is assumed to be the same as the mixing chemical potential of a chemically identical uncross-linked polymer of high molecular weight[3,27] and is given by

$$(\mu_1 - \mu_1^0)_m = RT[\ln \Phi_1 + \Phi_2 + \chi\Phi_2^2] \tag{12}$$

The Gibbs, ΔG_{el}, and Helmholtz, ΔA_{el}, free energy changes are assumed to be equivalent, since $P\Delta V$ is small at low pressures. Thus, given a theoretical expression for ΔA_{el}, the derivative specified in eq 9 may be readily calculated. As a simple illustration, if the James–Guth or phantom network expression

$$\Delta A_{el} = (\xi RT/2)(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{13}$$

is used, where ξ is the cycle rank of the network, one finds

$$\mu_{1,el} = \xi RTV_1/V^0\lambda \tag{14}$$

It will be noted that if ΔG_{el} is specified by any theory that conforms to the separability axiom, i.e., does not depend on the nature of the solvent, then the only solvent dependent term in $\mu_{1,el}$ is V_1. It is therefore convenient to divide this term out of eq 2. Furthermore, the λ factor in eq 14 is conveniently incorporated with the activity term to give the "reduced dilation modulus"[28]

$$G^d \equiv (\lambda/V_1) \ln (a_{1,c}/a_{1,u}) = (1/3RTV^0\lambda)(\partial \Delta G_{el}/\partial \lambda)_{T,P} \tag{15}$$

Returning to the example, eq 13, one has

$$G^d = (\lambda/V_1) \ln (a_{1,c}/a_{1,u}) = \xi/V^0 \tag{16}$$

if the James–Guth expression is assumed for ΔG_{el}. Of course, other free energy functions give different, in general deformation-dependent, reduced dilation moduli.

One reason for undertaking swelling measurements is to discriminate between these several theories. To do so, however, requires that the basic assumption of Flory and Rehner be valid. This, as we will see, proves not to be the case.

Differential Swelling

Traditional swelling experiments[29-31] are executed by placing a sample in a vessel containing a suitable solvent. The system is allowed to come to equilibrium, and the amount of solvent absorbed by the sample is measured by using gravimetric or volumetric methods. Since only one data point is obtained for a given temperature, an equilibrium measurement does not yield much insight into the elastic properties of the sample at different deformations.

In the experiments conducted by Gee, Herbert, and Roberts,[20] the vapor pressure and the mass of solvent absorbed by an elastomer were measured at constant temperature. The deflection of a platinum wire microbalance enabled either a mass difference measurement or an integral mass measurement to be made; these had to be done in separate experimental runs since there was only one balance in the system. The mass difference measurement was done by placing equal masses of cross-linked natural rubber and its uncross-linked analogue on opposing balance pans. The integral mass measurement was accomplished by placing only the cross-linked sample on one of the pans. A mercury thermometer was used to measure

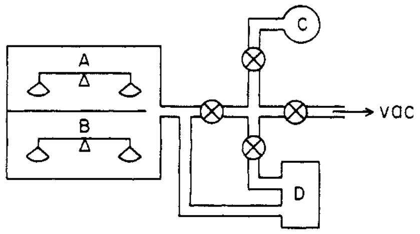


Figure 1. Experimental apparatus consists of a stainless-steel vacuum chamber containing two electronic balances, A and B. Balance A is loaded with a sample of the uncross-linked polymer, and balance B has a cross-linked polymer on one pan and an uncross-linked sample on the other pan. Integral sorption (balance A) is measured concurrently with differential sorption (balance B). The solvent reservoir is labeled C, and the capacitive diaphragm gauge is D.

the temperature, which was kept constant by using a well-stirred and well-lagged water bath.

Improvements on the design of the Gee apparatus were accomplished by Yen and Eichinger.[21,22] The improvements included a difference measurement on a precise electrobalance and a simultaneous integral mass measurement with a quartz helix. An uncross-linked sample and its cross-linked analogue were placed on opposing pans of the electrobalance. The readout from the electrobalance gave the difference of mass of diluent absorbed by the two samples. Employment of a calibrated quartz helix gave the total amount of solvent absorbed by an uncross-linked sample. When these two measurements are performed in parallel, the elastic chemical potential was obtained somewhat more directly than in the previous measurements. This same apparatus was used by Brotzman and Eichinger[23-25] in later experiments.

We have constructed a new all-steel and electronically instrumented apparatus for the measurements to be reported here. By so doing we have dramatically decreased the experimental uncertainties involved in the swelling measurements. Figure 1 shows a schematic of the apparatus. There are two sensitive balances, A and B, housed in a stainless-steel vacuum chamber that is connected by stainless-steel tubing to a solvent reservoir, C, and a pressure gauge, D. Gas flow is regulated by valves, ⊗. The terminus of the stainless-steel plumbing is a vacuum pumping station. The whole system, excluding the vacuum pumping station, is submerged in a constant temperature water bath during measurements.

The balances are sensitive electronic balances. Balance A is a Cahn 2000 electrobalance, which has a mass sensitivity of $\pm 0.1\ \mu g$; it is used for measuring the integral sorption on an uncross-linked polymer sample. Balance B is a Cahn RG electrobalance having a mass sensitivity of $\pm 2\ \mu g$. When the uncross-linked sample and its cross-linked analogue are placed on opposing pans of this balance, the mass difference of solvent absorbed by the two samples is obtained.

The pressure gauge, D, is an MKS capacitance diaphragm gauge with a pressure range of 0–108 Torr and a sensitivity of ±0.01 Torr. The valves are Nupro stainless-steel vacuum bellows regulating valves. Temperature regulation, using a Tronac temperature controller, kept the temperature constant to ±1 mK. A platinum resistance thermometer, manufactured by Minco, used in conjunction with a 6-digit calibrated Fluke multimeter, allowed for temperature measurements within ±1 mK.

The vacuum pumping station used to evacuate the system consists of a large capacity liquid nitrogen trap of our design, an Edwards diffusion pump, and an Edwards (or Leybold) rotary vane pump. The ultimate vacuum obtained was approximately 10^{-5} Torr. The system also contains several thermocouple gauges that operate in various ranges. These gauges are used to check the reference pressure during measurement and are not used for vapor pressure measurements.

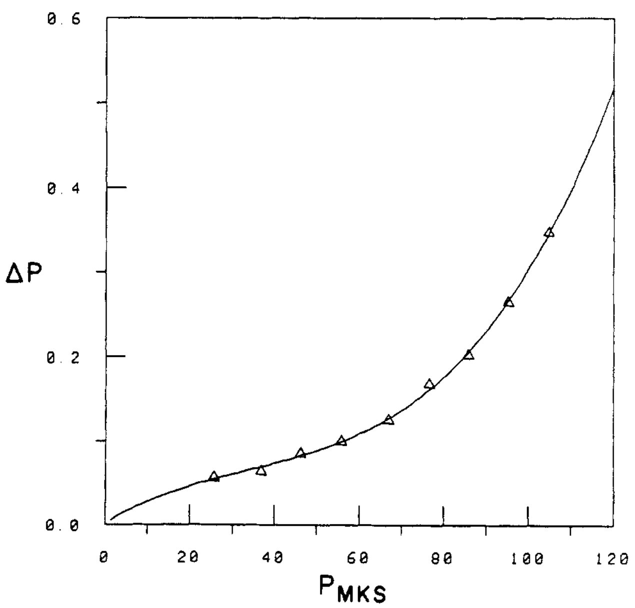


Figure 2. Plot of the calibration curve for the MKS gauge against a Ruska dead weight pressure gauge. The ordinate is $\Delta P = P_{\mathrm{MKS}} - P_{\mathrm{R}}$; the abscissa P_{MKS} is the pressure reading from the MKS gauge, and P_{R} is the actual pressure determined from the Ruska gauge. The Δ are the actual data points and the solid line is from a polynomial fit, using a third degree polynomial.

Calibrations

The calibration of the platinum resistance thermometer was performed by Minco Products Inc., of Minneapolis, MN (job 2-1305-01). The calibration was done at fixed-temperature points defined by IPTS-68 and by comparison with a platinum resistance thermometer certified by the National Bureau of Standards (NBS). The dependence of the resistance R_T of the thermometer at temperature T is given by

$$\begin{aligned} R_{\mathrm{T}} &= R_0(1 + AT + BT^2) \\ R_0 &= 100.05\Omega \\ A &= 3.9880 \times 10^{-3} C^{-1} \\ B &= -5.9970 \times 10^{-7} C^{-2} \end{aligned} \tag{17}$$

where R_0 (the resistance at 0 °C) and A and B are calibrated constants.

The Fluke multimeter was calibrated by Fluke, according to the requirements of MIL-STD-45662 using reference standards traceable to NBS, and had a tolerance of ±1 mΩ.

The MKS capacitance diaphragm gauge was calibrated by using a Ruska dead weight gas lubricated pressure gauge, Model 2465-71. A Ruska pressure gauge is a piston-cylinder assembly whose working faces are milled to a tolerance of $\pm 1 \times 10^{-6}$ in. The pressure developed by the gauge is given by

$$P = Mg/A \tag{18}$$

where M is the mass of the cylinder plus the mass of the added weight, g (= 9.80655 m/s^2) is the acceleration of gravity, and A (= 3.35640×10^{-4} m^2) is the area of the piston. The piston is referenced to NBS Test No. 215451. The weights are correct to 1×10^{-6} kg and are referenced to NBS No. 737/202491-60. Figure 2 shows a plot of the calibration curve, where $\Delta P = P_{\mathrm{MKS}} - P_{\mathrm{R}}$; P_{MKS} is the pressure from the MKS gauge, and P_{R} is the actual pressure as determined from the Ruska gauge. The triangles are the actual data, and the solid line was determined by using a polynomial of degree 3:

$$\Delta P = a_0 + a_1 P_{\mathrm{MKS}} + a_2 P_{\mathrm{MKS}}^2 + a_3 P_{\mathrm{MKS}}^3 \tag{19}$$

$a_0 = 0.173\,690 \times 10^{-2}$, $a_1 = 0.310\,384 \times 10^{-2}$, $a_2 = 0.542\,268 \times 10^{-4}$, and $a_3 = 0.533\,93 \times 10^{-6}$, where the a_i are the fitting parameters.

The Cahn 2000 was calibrated by zeroing the output of the balance with no load, then placing a class M 100-mg weight on the sample pan and adjusting the readout to 100 mg. Class M weights are described by the NBS Circular 547. The tolerance of the class M weights used is ±0.0054 mg and are traceable to NBS certificates. The linearity of the balance was checked by placing several other class M weights separately on the sample pan. There was no noticeable deviation from linearity.

The Cahn RG was calibrated by using class M weights using a much lengthier method than for the 2000 so as to adjust for unequal arm lengths of the balance beams. This calibration was done by placing various class M weights on opposing pans and by using the torque balance equation

$$(m_{\mathrm{l}} + x_{\mathrm{l}})l_{\mathrm{l}} = (M_{\mathrm{r}} + x_{\mathrm{r}})l_{\mathrm{r}} + C'R + B \tag{20}$$

to find the ratio of arm lengths. The subscripts l and r distinguish the left from the right side of the balance, the m_i are the masses of the class M weights, the x_i are the masses associated with the balance beams and sample holders, the l_i are the lengths of the balance beams, R is the balance reading, C' is a determined constant, and B is an arbitrary constant. The constants x and B are eliminated by doing a difference measurement, for which eq 20 yields

$$(m_{\mathrm{l}}' - m_{\mathrm{l}}'')l_{\mathrm{l}} = (m_{\mathrm{r}}' - m_{\mathrm{r}}'')l_{\mathrm{r}} + C'(R' - R'') \tag{21}$$

Setting $M_i = m_i' - m_i''$, $R = R' - R''$, and $r = l_{\mathrm{r}}/l_{\mathrm{l}}$ gives one the relation

$$M_{\mathrm{l}} = rM_{\mathrm{r}} + CR \tag{22}$$

where $C = C'/l_{\mathrm{l}}$. On multiplying eq 22 by M_{l} one obtains

$$M_{\mathrm{l}}^2 = rM_{\mathrm{r}}M_{\mathrm{l}} + CRM_{\mathrm{l}} \tag{23}$$

Equations 22 and 23 are summed and solved for r and C to give

$$r = \frac{l_{\mathrm{r}}}{l_{\mathrm{l}}} = \frac{\sum\limits_i M_{\mathrm{l}} \sum\limits_i RM_{\mathrm{l}} - \sum\limits_i R \sum\limits_i M_{\mathrm{l}}^2}{\sum\limits_i M_{\mathrm{r}} \sum\limits_i RM_{\mathrm{l}} - \sum\limits_i M_{\mathrm{r}}M_{\mathrm{l}} \sum\limits_i R} \tag{24}$$

$$C = \frac{\sum\limits_i M_{\mathrm{l}} - r\sum\limits_i M_{\mathrm{r}}}{\sum\limits_i M_{\mathrm{r}}} \tag{25}$$

With use of eq 24 and 25 the balance constants were found to be $r = 0.997\,68$ and $C = 0.998\,64$.

Experimental Section

Poly(dimethylsiloxane) (PDMS) was chosen for the experiments because it is stable, it has been studied extensively,[23-25,30,32-39] and it is commercially available in a range of molecular weights and end group functionalities. Two different cross-linked samples were chosen to test the contribution of the cross-links to the mixing free energy. The two elastomers were made with different cross-linkers, whose chemical structures are shown in Figure 3.

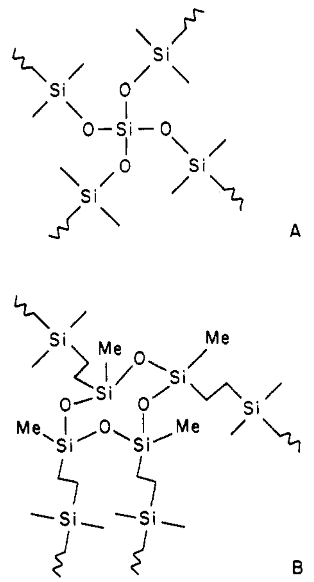
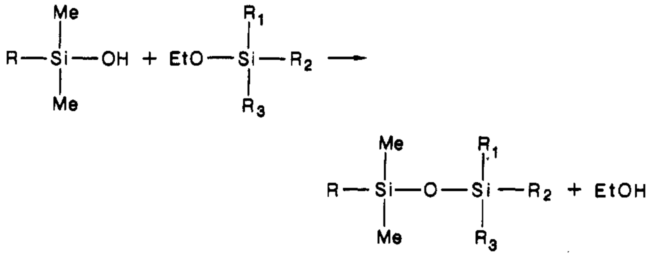


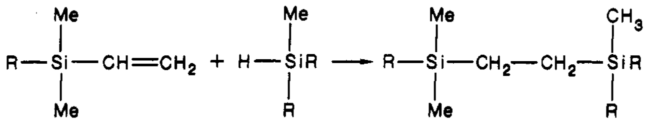
Figure 3. Diagram representing the structures of the two cross-linkers used. A is tetraethoxysilane used in conjunction with the hydroxy-terminated polymer. B is 1,3,5,7-tetramethylcyclotetrasiloxane, which was used with the vinyl-terminated polymer.

The $Si(OEt)_4$ cross-linker was used with a hydroxyl-terminated PDMS polymer. The reaction scheme for the cross-linker is



$$\mathrm{R{-}\overset{Me}{\underset{Me}{Si}}{-}OH + EtO{-}\overset{R_1}{\underset{R_3}{Si}}{-}R_2 \longrightarrow R{-}\overset{Me}{\underset{Me}{Si}}{-}O{-}\overset{R_1}{\underset{R_3}{Si}}{-}R_2 + EtOH}$$

where R represents the siloxane chain and R_1, R_2 and R_3 are ethoxy groups. A vinyl-terminated PDMS monomer was used with the cyclic cross-linker; the reaction scheme for cross-linking is



$$\mathrm{R{-}\overset{Me}{\underset{Me}{Si}}{-}CH{=}CH_2 + H{-}\overset{Me}{\underset{R}{Si}}R \longrightarrow R{-}\overset{Me}{\underset{Me}{Si}}{-}CH_2{-}CH_2{-}\overset{CH_3}{\underset{R}{Si}}R}$$

The monomer used in both systems had a molecular weight of 26 000. In ideal circumstances the two networks should be identical, except for the structure of the cross-linkers, and they should have the same modulus of elasticity. If the cross-link–solvent interaction is significant, these samples should show different swelling behavior.

The uncross-linked PDMS samples were kindly provided by Prof. J. E. Mark and by General Electric. The Mark sample contained 0.5 mol % (methylvinyl)siloxane units and had a molecular weight of approximately 5×10^5. The GE sample (DSRE 3367) had a molecular weight of about 1×10^6. Both samples were fractionated from a 1% solution in cyclohexane using acetone as the precipitate at 25 °C. The temperature was kept constant during precipitation by using a large, well-stirred bath.

The $Si(OEt)_4$ cross-linked sample was prepared in a drybox by placing 40 mg of $Si(OEt)_4$, 10.0013 g of silanol-terminated PDMS (M_n = 26 000), and 40 mg of tin(II) 2-ethylhexanoate (all from Petrarch) in a beaker and stirring vigorously for a few minutes. The contents of the beaker were poured into a Teflon mold of dimensions 1.5 mm × 9 cm × 4 cm. The mold was placed in a vacuum box at room temperature for several days to allow the cross-linking reaction process to be completed.

The cyclic cross-linked PDMS was prepared in a drybox by placing 10.00 g of vinyl-terminated PDMS (M_n = 26 000), 30.00 mg of 1,3,5,7-tetramethylcyclotetrasiloxane, and 4 mg of a 5%

Table I
Characterization of Model Network Samples

end group	MW	cross-linker	[X]/[E][a]	sol frac
vinyl	26000	c-$(HSiCH_3O)_4$[b]	1.3	9.02%
silanol	26000	$Si(OEt)_4$[c]	1.0	4.70%

[a] Ratio of concentrations of cross-link functional groups to the chain ends. [b] Reaction conditions: 150 °C in drybox with chloroplatinic acid as catalyst. [c] Reaction conditions: room temperature, under vacuum, with 1 ppt tin(II) 2-ethylhexanoate as catalyst.

solution of chloroplatinic acid in PDMS (all from Petrarch) in a beaker and then stirring vigorously for several minutes. The contents of the beaker were placed on a Teflon casting plate of dimensions given above. The plate was placed on a 1 in. thick piece of aluminum which together were placed on a hot plate. A thermocouple was attached to the piece of aluminum, and the temperature was elevated to 150 °C. This assembly was kept in the drybox for 2 days to allow the PDMS sample to cure.

The sol was extracted from each of the samples by placing them in a 500-mL round-bottom flask that contained acetone and 1% cyclohexane. The concentration of the cyclohexane was increased in small increments over several days until the concentration reached 100%. The elastomers were swollen at a slow rate so as to reduce the chance of rupturing the network by osmotic shock. The cyclohexane was discarded, and fresh cyclohexane was added several times over a few days to remove all the sol. To deswell the sample, the above process was reversed until a 100% acetone solution was obtained. The sample was removed from the vessel and allowed to dry completely. The sol fraction was determined from the initial and final dry weights. Table I summarizes the characterization of the two cross-linked systems.

The samples and pans for use with the electrobalances were prepared by using the following method. The pans were weighed on a Cahn 27 electrobalance. The samples were trimmed by using tweezers and surgical scissors so that they were within a few hundredths of a milligram of each other. The samples were then placed on their respective pans and were weighed. The sample pans containing the uncross-linked PDMS samples were placed on the sample side of the Cahn 2000 and Cahn RG. The sample pan containing the cross-linked sample was placed on the tare side of the RG. The system was sealed and then evacuated. After a vacuum of 10^{-4} Torr was obtained (which required a few days of continuous pumping) the water bath was raised and the system was isolated.

Measurements were done in the following manner for each sample. The pump was isolated from the system by closing a shutoff valve. An increment of solvent was added to the sample chamber while the increase in pressure was noted on the MKS gauge. The pressure increase was ~5 Torr at 30 °C and ~3 Torr for the 20 °C measurements. The system was allowed to come to equilibrium, which required anywhere from 4 to 24 h, as judged by the flatness and regularity of the trace on the two-pen recorder that recorded the output from both the RG and 2000 balances. The temperature, pressure, and both balances' mass readouts were recorded. The above procedure was repeated until the pressure in the system reach 105 Torr for the 30 °C measurements and about 70 Torr for the 20 °C measurements. The system was evacuated and then checked for possible leakage. Desorption measurements were conducted during solvent removal to check for sample hysteresis; none was observed.

Data Analysis

The uncorrected mass difference, ΔM_1, as given directly from the RG mass readout is

$$\Delta M_1 = M_{1u} - M_{1c} \tag{26}$$

where M_{1u} and M_{1c} are the mass of the solvent absorbed by the uncross-linked and cross-linked PDMS samples, respectively, at solvent activity a_1. The activity of solvent is determined by

$$a_1 = P/P^0 \tag{27}$$

where P ($= P_{mks} - \Delta P$) is the corrected pressure from the MKS gauge (see calibration section) and P^0 is the equilibrium vapor pressure at temperature T as given in Table II. The volume fraction Φ_{1u} of solvent with respect to the uncross-linked sample is calculated from

Table II
Physical Properties of Polymer and Solvents

substance	temp (°C)	density (g/cm³)	p^0
PDMS[a]	20	0.9742	
	30	0.9653	
benzene[b]	20	0.8790	75.203
	30	0.8685	119.338
cyclohexane[c]	20	0.7786	77.519
	30	0.7693	121.726

[a] Reference 41. [b] Reference 62a. [c] Reference 62b.

$$\Phi_{1u} = \frac{M_{1u}'/\rho_1}{M_{1u}'/\rho_1 + M_{2u}'/\rho_2} \tag{28}$$

where M_{1u}' is the mass of the solvent absorbed by the uncross-linked sample as determined by the Cahn 2000 balance and M_{2u}' is the dry mass of the polymer. The densities of the solvent and polymer, ρ_1 and ρ_2, respectively, are given in Table II.

The corrected mass of the solvent, M_{1c}, absorbed by the cross-linked sample is determined by

$$M_{1c} = \frac{M_{1u} - C\Delta M_1}{r} \tag{29}$$

with

$$M_{1u} = \frac{M_{2u}}{M_{2u}'} M_{1u}' \tag{30}$$

Here M_{1u} is the mass of solvent absorbed by the uncross-linked sample (dry mass M_{2u}) that is on the RG balance. The parameters C and r in eq 29 are the balance constant and arm length ratio for the RG (see eq 24 and 25). The volume fraction of the solvent for the cross-linked PDMS is given by eq 28 with subscript u replaced by c.

The volume fraction difference, $\Delta\Phi_1$, is defined as

$$\Delta\Phi_1 = \Phi_{1u} - \Phi_{1c} \tag{31}$$

The first five data points of $\Delta\Phi_1$ vs Φ_c were fitted to a linear equation by means of a least-squares fitting routine. With use of the intercept, the values of Φ_{1c} were adjusted by a small amount so as to ensure that $\Delta\Phi_1$ passed through the origin. The adjustments were well within the experimental uncertainty. The $\Delta\Phi_1$ vs Φ_{1c} data were then fitted to a polynomial of lowest degree (either 3 or 4) using a fitting routine.[40] The weighting used in the fitting routine was either statistical, $(1/\Delta\Phi_1)$, equal weights, or instrumental, $(1/\sigma_{\Delta\Phi_1})$. The values for $\sigma_{\Delta\Phi_1}$ were determined from error propagation formulas:

$$\sigma_{\Delta\Phi_1}{}^2 = \left[\left(\frac{\partial\Delta\Phi_1}{\partial\Phi_{1u}}\right)^2 \sigma_{\Phi_{1u}}{}^2 + \left(\frac{\partial\Delta\Phi_1}{\partial\Phi_{1c}}\right)^2 \sigma_{\Phi_{1c}}{}^2\right] \tag{32}$$

where

$$\sigma_{\Phi_{1c}}{}^2 = \left(\frac{\partial\Phi_{1c}}{\partial M_{1c}}\right)^2 \sigma_{M_{1c}}{}^2 + \left(\frac{\partial\Phi_{1c}}{\partial M_{2c}}\right)^2 \sigma_{M_{2c}}{}^2 + \left(\frac{\partial\Phi_{1c}}{\partial\rho_1}\right)^2 \sigma_{\rho_1}{}^2 + \left(\frac{\partial\Phi_{1c}}{\partial\rho_2}\right)^2 \sigma_{\rho_2}{}^2 \tag{33}$$

$$\sigma_{\Phi_{1u}}{}^2 = \left(\frac{\partial\Phi_{1u}}{\upsilon M_{1u}}\right)^2 \sigma_{M_{1u}}{}^2 + \left(\frac{\partial\Phi_{1u}}{\partial M_{2u}}\right)^2 \sigma_{M_{2u}}{}^2 + \left(\frac{\partial\Phi_{1u}}{\partial\rho_1}\right)^2 \sigma_{\rho_1}{}^2 + \left(\frac{\partial\Phi_{1u}}{\partial\rho_2}\right)^2 \sigma_{\rho_2}{}^2 \tag{34}$$

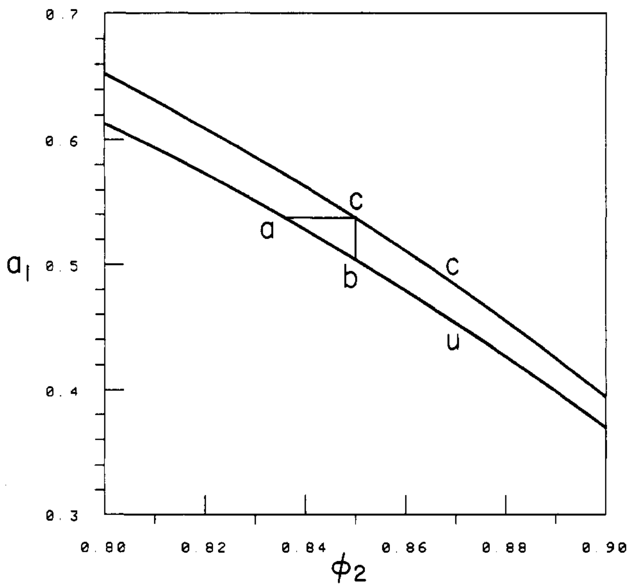


Figure 4. Representative solvent activity a_1 vs volume fraction of polymer Φ_2 calculated with fictitious parameters described in the text. The measurements give points a and c, and the data analysis described in the text gives point b. The ratio of activities at points c and b is required to construct the dilation modulus. Curves for the cross-linked and uncross-linked polymers are labeled c and u, respectively. Note the expanded scale.

The Flory interaction parameter χ was determined from the Flory–Huggins equation

$$\chi = \frac{\ln (a_{1u}/\Phi_{1u}) - \Phi_{2u}}{\Phi_{2u}^2} \tag{35}$$

The χ vs Φ_{2u} values were fitted to linear least-squares equations to obtain χ_0 and χ_1, where

$$\chi = \chi_0 + \chi_1 \Phi_{2u} \tag{36}$$

To aid the reader in the discussion of the data reduction, a representative plot of activity of the solvent vs the volume fraction of polymer is shown in Figure 4 for cross-linked (c) and uncross-linked (u) polymers. The activity was calculated from the equation

$$a_1 = (1 - \Phi_2) \exp[\Phi_2 + \chi \Phi_2^2 + A \Phi_2^{1/3}] \tag{37}$$

with $\chi = 0.5$ and with (i) $A = 0$ (linear chains) and (ii) $A = 1/15$ (network, using the James–Guth expression, see eq 13). The point c represents the activity a_{1c} of solvent above the cross-linked polymer for a given volume fraction Φ_{2c}. Point a represents the volume fraction, Φ_{2u}, of the uncross-linked sample when $a_{1c} = a_{1u}$. Point b represents the activity, a_{1u}, of the uncross-linked polymer when $\Phi_{2u} = \Phi_{2c}$.

Turning now to the actual data analysis, but using this figure as a guide, the dilation modulus is determined by calculating the logarithm of the ratio of activities, represented by points c and b in Figure 4, of the solvent above the cross-linked and uncross-linked PDMS samples. The activity of the solvent at point c is the same as at point a. It is determined by using the Flory–Huggins equation

$$a_{1c} = (1 - \Phi_{2u}) \exp[\Phi_{2u} + (\chi_0 + \chi_1 \Phi_{2u}) \Phi_{2u}^2] \tag{38}$$

where Φ_{2u} is determined from the smoothed $\Delta\Phi_1$ vs Φ_{1c} data according to

$$\Delta\Phi_1 = \Phi_{1u} - \Phi_{1c} = \Phi_{2c} - \Phi_{2u} \tag{39}$$

The activity a_{1u} at point b is calculated from

$$a_{1u} = (1 - \Phi_{2c}) \exp[\Phi_{2c} + (\chi_0 + \chi_1 \Phi_{2c}) \Phi_{2c}^2] \tag{40}$$

where $\Phi_{2c} = \Phi_{2u}$ is the volume fraction of the polymer at points c and b. The reduced dilation modulus, G^d, is then calculated by using the values a_{1c} and a_{1u} from eq 38 and 40 with the use of the left member of eq 16, i.e.

$$G^d = \frac{\lambda}{V_1} \ln \frac{a_{1c}}{a_{1u}} \tag{41}$$

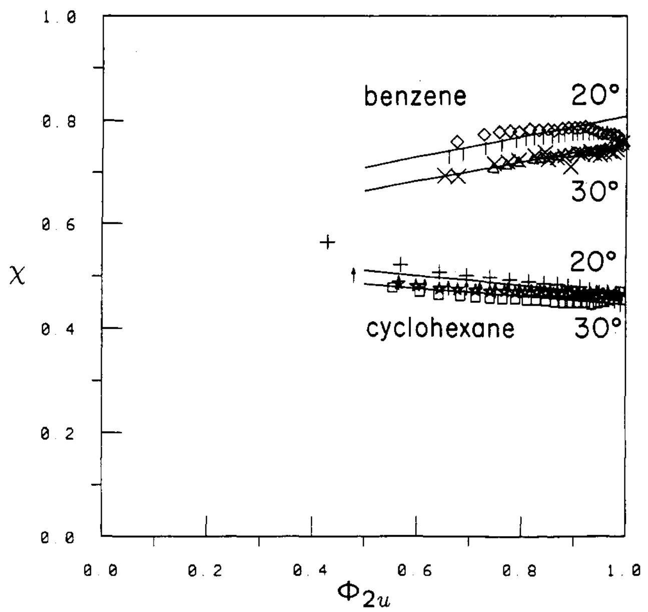


Figure 5. Flory–Huggins interaction parameters for the General Electric (GE) and J. E. Mark uncross-linked PDMS samples measured in benzene and cyclohexane, both at 20 and 30 °C. The diamond, X, +, and square symbols represent data from the GE sample, and the |, Δ, ↑ and star symbols represent those from the Mark sample.

Results and Discussion

The Flory–Huggins interaction parameters χ for the two uncross-linked samples are presented graphically as plots of χ vs Φ_{2u} in Figure 5. The data represented by the figure are from eight separate runs: each sample was swollen in two different solvents, benzene and cyclohexane, at two different temperatures, 20 and 30 °C. Each of the four solid lines in the figure was generated by combining measurements, under like conditions, of the GE and Mark samples and using a weighted least-squares analysis to obtain coefficients of eq 36. The weights were calculated from a propagation of errors of the general form

$$\sigma_\chi^2 = \left(\frac{\partial \chi}{\partial \Phi_{2u}}\right)_{a_{1u}} \sigma_{\Phi_{2u}}^2 + \left(\frac{\partial \chi}{\partial a_{1u}}\right)_{\Phi_{2u}} \sigma_{a_{1u}}^2 \tag{42}$$

The range of values of σ_χ is 0.001–0.07 for Φ_{2u} ranging from 0.72 to 0.991.

The equation for the least-squares fit of χ for PDMS + benzene at 30 °C is

$$\chi = 0.5724 + 0.1840\Phi_2 \tag{43}$$

These results are the same, within experimental error, as those of Brotzman and Eichinger[23-25] and in good agreement with Shih and Flory[41] and Yen and Eichinger.[21]

The equation for the least-squares fit through the PDMS + cyclohexane data measured at 30 °C is

$$\chi = 0.5230 - 0.0772\Phi_2 \tag{44}$$

The data are well within the reproducibility observed by others for the PDMS + cyclohexane system.[23-25,41,42]

The equation for the 20 °C measurements are as follows: for benzene

$$\chi = 0.6104 + 0.1992\Phi_2 \tag{45}$$

and for cyclohexane

$$\chi = 0.5600 - 0.0980\Phi_2 \tag{46}$$

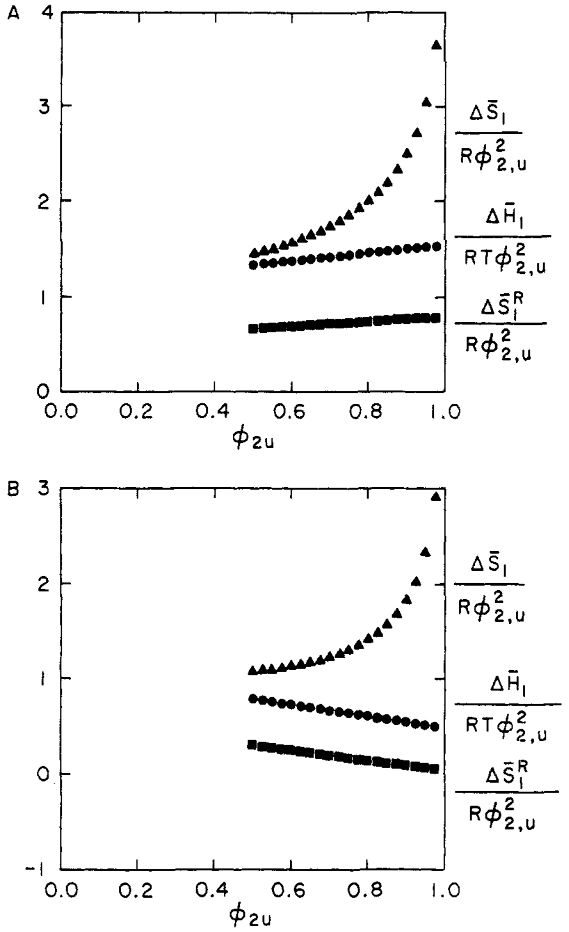


Figure 6. (A) Plots of the reduced thermodynamic functions vs volume fractions for the benzene measurements. PDMS + benzene at the mean temperature of 25 °C. (B) Same as above but for cyclohexane.

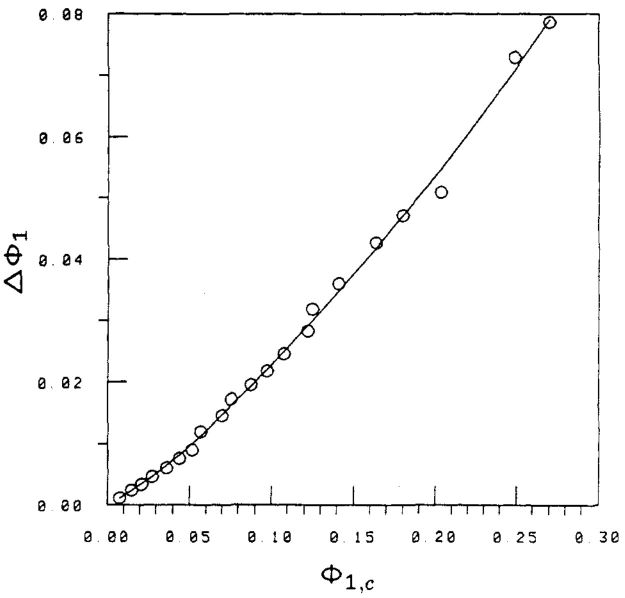


Figure 7. $\Delta\Phi_1$ vs $\Phi_{1,c}$ for the $Si(OEt)_4$ cross-linked sample in benzene at 30 °C.

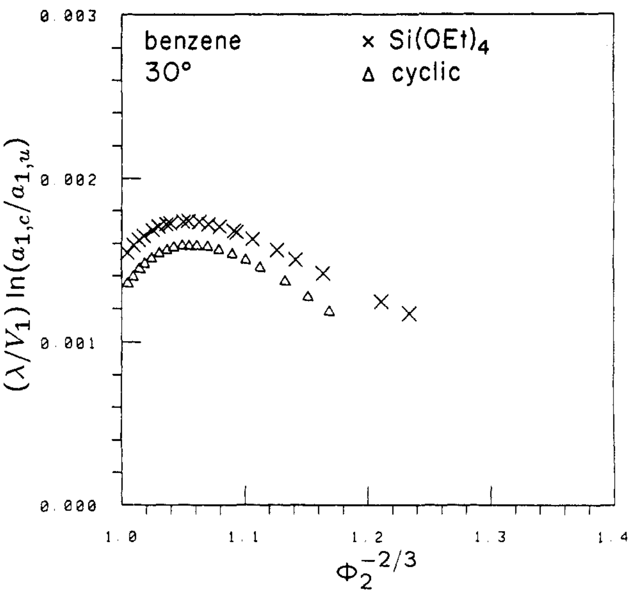


Figure 8. Reduced dilation moduli of $Si(OEt)_4$ cross-linked and 1,3,5,7-tetramethylcyclotetrasiloxane cross-linked PDMS at 30 °C. The dimensions of $G^d = (\lambda/V_1)\ln(a_{1,c}/a_{1,u})$ in this figure and in Figures 9–13 are mol/cm^3.

Currently this is the only 20 °C χ data available for these polymer concentrations of PDMS.

Figure 6 shows plots of the reduced thermodynamic functions vs Φ_2 for the benzene and cyclohexane systems. The values of the enthalpy parameter $\chi_H = \bar{H}_1/RT\Phi_2^2 = -T(\partial\chi/\partial T)_{p,\Phi_2}$ for both systems are positive; that for benzene is 2–3 times larger than that for cyclohexane. This is in rough agreement with the values of ΔH_m at infinite dilution measured by Delmas et al.[43] and by Morimoto.[44] The measured values of ΔH_m are 5.2 J/g[43] for cyclohexane and 14.2[43] and 11 J/g[44] for benzene. The values of $\chi_S = -\bar{S}_1^R/R\Phi_2^2 = \chi - \chi_H$ for both systems are negative. Also shown in Figure 6 are values of the reduced partial molar entropy of dilution, defined by

$$\Delta\bar{S}_1/R\Phi_2^2 = -[\ln\Phi_1 + \Phi_2]/\Phi_2^2 + \bar{S}_2^R/R\Phi_2^2 \quad (47)$$

Shih and Flory[41] report positive values of χ_S at infinite dilution.

Upon comparison of our data with that of Shih and Flory,[41] Brotzman and Eichinger,[23-25] and Kuwahara et al.,[42] it becomes apparent that χ vs Φ_2 shows a large amount of curvature for $\Phi_2 < 0.5$ for both cyclohexane and benzene. The interaction parameter χ for cyclohexane appears to have a maximum at $\Phi_2 \cong 0.5$. Thus, linear extrapolation of our χ_S data to $\Phi_2 = 0$ would not give comparable results.

One representation data set of measured solvent volume fraction differences, $\Delta\Phi_1$, is plotted as a function of Φ_{1c} in Figure 7. The solid curve in Figure 7 is a fourth degree polynomial. Seven of the data sets were fitted to fourth degree polynomials, and one was fitted to a third degree polynomial. The polynomials were determined by a weighted least-squares analysis[40] and were constrained to pass through the origin. The smoothed $\Delta\Phi_1$ vs Φ_{1c} data were then used to obtain the dilation modulus, G^d, as specified in the data analysis section.

The reduced dilation moduli for the PDMS networks measured at 30 °C are presented in Figures 8–11. Figures 8 and 9 show the results for the two samples swollen in benzene and cyclohexane, respectively. In both figures the symbol × represents the $Si(OEt)_4$ cross-linked sample and the symbol Δ represents the cyclic cross-linked sample. The solvent dependence of the dilation moduli of the samples is shown in Figures 10 and 11 for the $Si(OEt)_4$ and the cyclic cross-linked samples, respectively. In both of these figures, the symbol × represents the benzene measurements and the symbol Δ represents the cyclohexane measurements.

The two samples do not show identical behavior in a given solvent at fixed temperature as shown by Figures 8

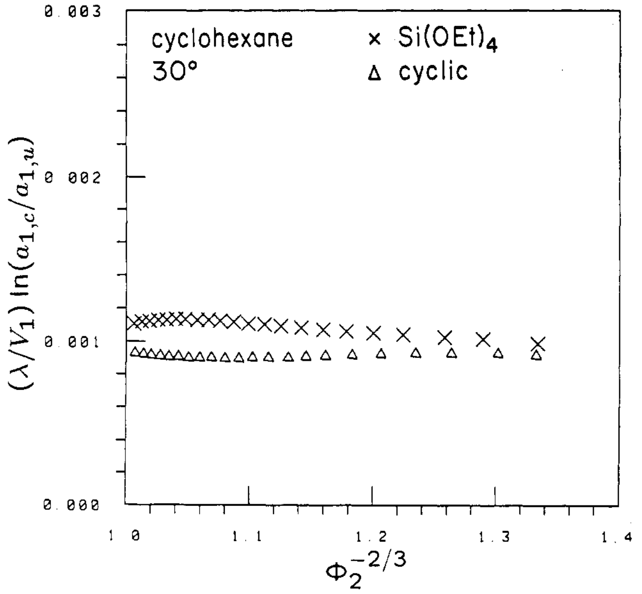


Figure 9. Reduced dilation moduli for the same two elastomers as in Figure 8, but swollen in cyclohexane at 30 °C.

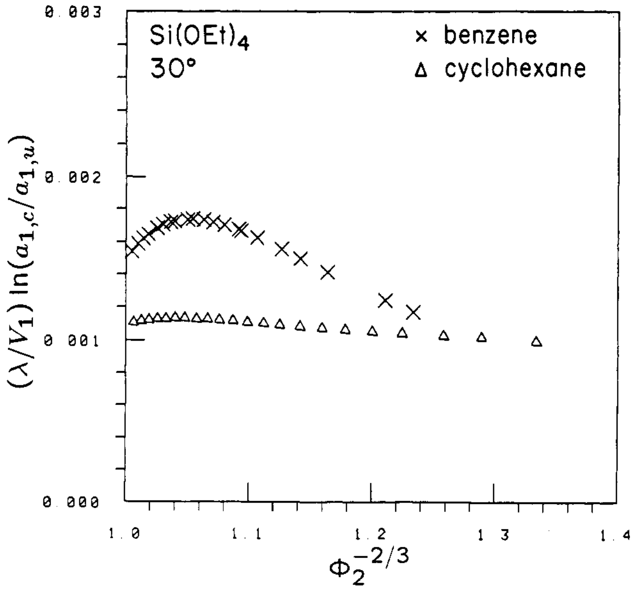


Figure 10. Reduced dilation moduli for the $Si(OEt)_4$ cross-linked elastomer swollen with benzene and cyclohexane.

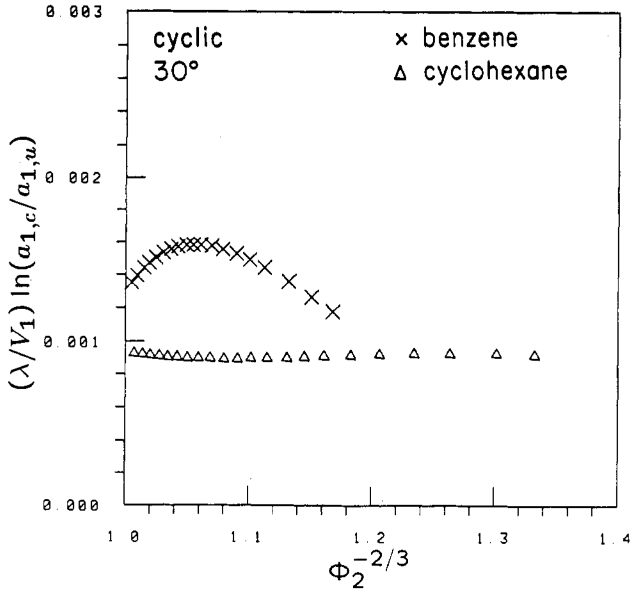


Figure 11. Reduced dilation moduli for the cyclic cross-linked elastomer swollen with benzene and cyclohexane at 30 °C.

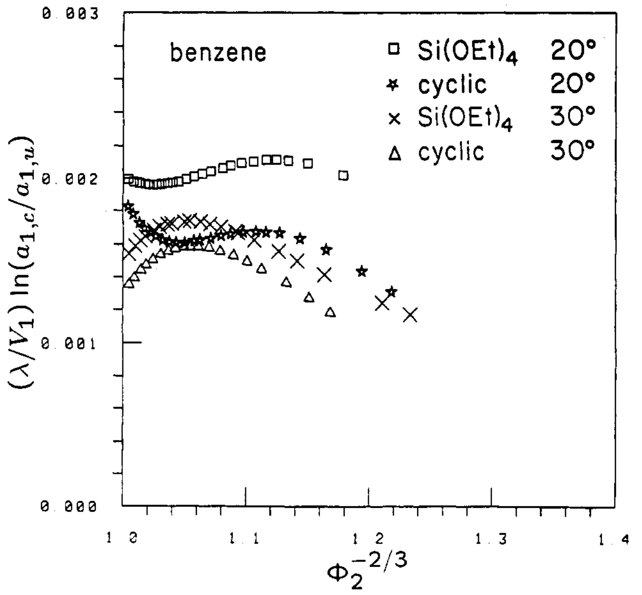


Figure 12. Temperature dependence of the dilation moduli. The two elastomers were swollen in benzene at 20 and 30 °C. The data for 30 °C are the same as those in Figure 8.

and 9. This is doubtless a reflection of the different sol fractions found for the two samples (see Table I). The sol fraction of the $Si(OEt)_4$ sample was 4.7% and that for the cyclic sample was 9.02%. This sol fraction difference is likely due to the known side reactions that accompany the hydrosilation reaction.[45,46] Calculations[47] and experiments[48] show that a larger sol fraction leads to a smaller modulus when all other factors are equal. It appears that the curves could be scaled on the ordinates to become identical (for a given solvent) to within experimental uncertainty. This scale factor should be proportional to the modulus of elasticity according to all known theories of elasticity.

To make these suppositions more concrete, one may inspect Figures 8, 9, 12, and 13 (the latter two yet to be discussed) to reveal that the reduced dilation moduli for the two elastomers under like conditions differ from one another by factors ranging from 8% to 22%, with the average being about 16%. On interpolating computer simulation results for tetrafunctional end-linked PDMS networks[47] to the physical parameters pertinent to these experiments, i.e., $M = 26\,000$, sol fractions of 4.7% and 9.0%, one finds that the cycle ranks differ by about 23%. The measured differences are thus comparable to values gleaned from network structure studies, while at the same time it is noteworthy that the computer results, which do not incorporate entanglements, overestimate the observed differences. Whether or not this is significant in light of the failure of the experiments to conform to any theory is an open question.

Admittedly, an anomaly of the magnitude that we observe may call to question this assumed proportionality to the modulus. Unfortunately, there is little else that we may invoke to explain the differences between the curves. The fact that we have not made identical networks, apart from the structure of the cross-links, must not detract from our main conclusion. On the contrary, the fact that the *qualitative* features of the swelling curves are unaffected by network imperfections supports our conclusion that the solvent dependence that we observe is not a function of the details of network structure but is instead a generic phenomenon dependent on subtleties of the solvent–net-

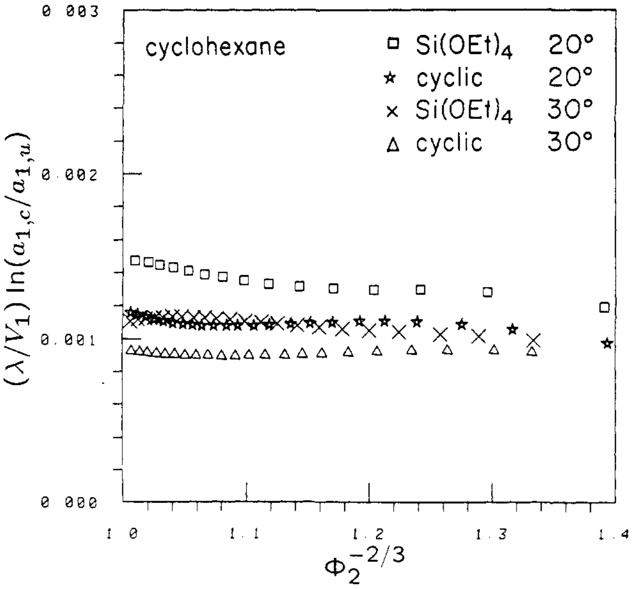


Figure 13. Temperature dependence of the dilation moduli in cyclohexane. The two elastomers were swollen at 20 and 30 °C. The data for 30 °C are the same as those in Figure 9.

work interactions that are not yet comprehended in theory.

It is clear from Figures 10 and 11 that the dilation moduli are solvent-dependent. The benzene results have a pronounced maximum at $\Phi_{2u}^{-2/3} \cong 1.05$ where the cyclohexane values are, for all practical purposes, independent of Φ_{2u}. This behavior conflicts with the Flory–Rehner additivity assumption; the measured dilation moduli should not depend upon the solvent. Brotzman[24] and Yen[22] observed the same discrepancy in their measurements using a different apparatus.[22]

As mentioned earlier, this breakdown in additivity could be caused by an interaction parameter that is different for the cross-links than for the midchain segments. The two polymer systems used in our measurements have cross-links that are structurally quite different (see Figure 3). Any contribution from the cross-links to the interaction parameter would be detected by a significant difference in the dilation moduli for the two networks swollen with a given solvent. However, since the behavior in benzene differs from that in cyclohexane in just the same way for the two samples proves, beyond a reasonable doubt, that a mixing term for the cross-links does not contribute to the breakdown in additivity.

When these new data are compared with those reported by Brotzman and Eichinger,[24,25] it is noted that there are differences that deserve to be explained. Unfortunately, we are unable to arrive at a full explanation of the differences. Two of the end-linked PDMS samples[24] that were investigated by Brotzman are nominally the same as the samples used here except for the molecular weight between cross-links. Yet the dilation moduli measured in the previous work are smaller by a factor of nearly 5. This is traceable to the raw data; the $\Delta\Phi$ vs $\Phi_{2,c}$ data recorded in the previous study[24] are smaller by factors of 3–5 than those reported here. We have always taken great pains to calibrate the Cahn balance that has been used in these measurements, and it is hard to imagine how a systematic error of such a magnitude could arise. The fact that the χ data gathered here for benzene agrees perfectly with the previous data and that the cyclohexane data are in close accord, suggests that the pressure measurements and integral mass measurements are not subject to systematic error. (For reasons that are not at all clear, cyclohexane is a problematic solvent. We have always experienced greater difficulties in reproducing measurements with cyclohexane than with other common solvents. And this is true of integral sorption, not just differential sorption. The only thing that comes to mind that might possibly explain this is a perturbation of the chair–boat conformational equilibrium of C_6H_{12} that is dependent on solution composition or even on the composition of vacuum chamber components.)

We think that the most likely source of the quantitative differences between this study and the previous ones is to be found in the sample differences. We do not understand the source of departures from theory in detail and so are inclined to believe that differences in samples can give rise to the different results that are observed. Both of the samples used here came to swelling equilibrium at room temperature in cyclohexane at ca. 0.14 volume fraction of polymer. This is close to the value of 0.146 found previously[24] for the sample nearest in characteristics to those used here. More will be said on this point later.

The absence of a cross-link–solvent interaction term is supported by measurements by Candau et al.[49] They studied the polymer–solvent interaction parameter of linear, comb, and star-branched polystyrenes and found that the structural dependence of χ disappears at polystyrene volume fractions >0.1. Our measurements were conducted at $\Phi_2 > 0.5$. Even at lower concentrations ($\Phi_2 < 0.1$), the difference between the interaction parameter for stars (the node of a star resembles a cross-link) and linear chains was at most 10%. Calculations put forward by Brotzman[24] demonstrate that the difference in the interaction parameters must be much larger than 10% if they are to account for the apparent solvent dependence.

Figures 12 and 13 depict the temperature dependence of the dilation moduli for the two networks in benzene and cyclohexane. Theories predict that the modulus is proportional to RT and hence that $(\lambda/V_1)\ln(a_{1,c}/a_{1,u})$ is independent of temperature, except for a small temperature dependence due to that of $\langle r^2\rangle_0$[50,51] or V^0. The measured dilation moduli at 20 °C are larger than those at 30 °C, especially at larger swelling ratios where the data are most reliable. This suggests that $\mathrm{d}\langle r^2\rangle_0/\mathrm{d}T$ is positive,[52] which is indeed the correct sign; the measured temperature coefficient of the unperturbed dimensions of PDMS is positive.[52] However, the magnitude of the temperature dependence is larger than that obtained from stress-strain measurements,[53] where the measured f/T change was 1% from 293 to 303 K. Our measurements show a 6% change in G^d for the cyclic sample swollen in benzene and a 20% change in G^d for the other systems. It appears that the magnitude of the temperature dependence in our measurements cannot be ascribed solely to $\mathrm{d}\{r^2\}_0/\mathrm{d}T$.

The positions of the maxima of the benzene dilation moduli appear to be temperature dependent. The maximum shifts from $\Phi_2^{-2/3} = 1.05$ at 303 K to $\Phi_2^{-2/3} = 1.12$ at 293 K for both samples. This shift cannot be explained by any of the current theories; most of the theories do not even predict a maximum.

The curves representing the 20 °C benzene dilation moduli could be scaled on the ordinate to become identical, within experimental uncertainty. However, the scaling factor would be larger than that needed to scale the other curves. Each pair of curves representing the $Si(OEt)_4$ and the cyclic samples' dilation moduli, measured in cyclohexane at 20 and 30 °C and in benzene at 30 °C, could be scaled on the ordinate to become identical by using nearly the same scaling factor. This discrepancy in the scaling factor for the 20 °C benzene data, along with the fact that the maximum dilation modulus for the cyclic sample with benzene at 20 °C is only 6% larger than at 30 °C, while the other systems show a 20% larger dilation modulus at 20 °C than at 30 °C, gives reason to believe that the measured dilation modulus for the benzene + cyclic sample at 20 °C is too low. This result, when coupled with the $\Delta\Phi_1$ data (not shown, but which appear to be significantly less smooth than those of the other runs), suggests that this data set is plagued by larger experimental uncertainty than the others.

Comparisons with Theories

Any attempt to derive molecular parameters from theories of elasticity that conform to the separability hypothesis is doomed to failure. Nonetheless, it is instructive to see just how wide of the mark this data analysis can be. We here present illustrative calculations of M_c, the molecular weight between cross-links, on the basis of several different theories of elasticity.

The James–Guth or phantom network theory fits the cyclohexane data reasonably well. Setting $G^d = \xi/V^0 = 0.0012$ (see eq 16 and Figure 13) and $\xi/V^0 = \rho/2M_c$[54] gives $M_c = 406$ g/mol. The Mooney–Rivlin equation[13,32,55–57] for G^d is

$$G^d = (2/RTV^0)(C_1 - C_2/\lambda^4)$$

where C_1 and C_2 are the standard Mooney–Rivlin parameters. This equation does not follow any of the swelling data. However, if one adjusts the parameters so that the theoretical curve crosses the cyclohexane data at about $\Phi_2^{-2/3} \simeq 1.1$, it is found that $C_1/RTV^0 = 0.002$ and $C_2/RTV^0 = 0.0015$ are as rational as other choices for the parameters. If one now sets $C_1/RTV^0 = C\rho/2M_c$, where $C = 0.065$,[32] one finds $M_c = 158$ g/mol. The Flory–Tatara[58] equation gives approximately the same result, and Wall–Flory[9–13] gives M_c about twice as large (owing primarily to the difference of a factor of 2 between Wall–Flory and James–Guth theories).

The Flory–Erman[52,54,59] theory fits the 20 °C benzene data reasonably well with the parameter values: $\xi/V^0 = 4.09 \times 10^{-4}$, $\kappa = 1.0$, and $\zeta = 90$. (This value of ζ is unreasonably large compared with that required to fit stress–strain data.) This value of $\xi/V^0 = \rho/2M_c$ gives $M_c = 1190$ g/mol.

Thus, values of M_c ranging from 406 to 1190 g/mol can be deduced from the data by applying theories that give the best fits, namely, James–Guth theory for the cyclohexane data and Flory–Erman theory for the benzene data. The actual M_c is 26 000 g/mol. This large discrepancy speaks for itself.

The only theoretical treatment of elasticity known to us that predicts nonadditivity is that of Ball and Edwards.[60] We have not attempted to analyze these data with the Ball–Edwards equations because it is not clear at the present time that the ranges of parameters for which the calculations were done are appropriate to these experiments.[61]

Conclusion

The Flory–Rehner theory is in need of modification to account for the solvent dependence of the dilation modulus. The data that has been presented for the two cross-linked samples swollen in two different solvents show that the solvent dependence is not due to a difference in the interaction parameters of cross-links and midchain segments.

The solvent dependence is doubtless due to some sort of mixing-elastic cross-term. Because the magnitude of the observed differences between the cyclohexane and benzene isotherms is so large, it is likely that the cross-term is additive rather than a simple multiplicative adjustment to the modulus, vis-à-vis Flory's thermodynamic cycle. A multiplicative term could arise from a solvent dependence of the standard state dimensions of the molecules. However, it is difficult to see how this could amount to more than a small scaling factor on the ordinate. According to the Ball–Edwards theory,[60] the density fluctuations in the network are suppressed relative to those in a solution of linear chains at like concentration, and this effect leads to additive terms. The magnitude of the density fluctuations is determined by the strength of the pseudopotential that acts between polymer segments. This, in turn, is given by the second derivative of the mixing free energy density. Since there is a $1/\phi_1$ term in this derivative, the fluctuation contribution to the free energy is largest for small amounts of added solvent. It might be that the Flory–Rehner theory is most nearly correct at swelling equilibrium and that departures from additivity are most pronounced at small swelling ratios. Whatever is the ultimate explanation of the questions raised by these experiments, it is apparent that the elastic free energy of an isotropically swollen elastomer cannot be evaluated without a viable theory. We hope to continue these measurements with other systems to explore the thermodynamic variables that influence the results.

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Registry No. Si(OEt)$_4$, 78-10-4; tetramethylcyclotetrasiloxane, 2370-88-9.

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Integral Equation Theory of Polymer Melts: Intramolecular Structure, Local Order, and the Correlation Hole[†]

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ABSTRACT: Our previously proposed microscopic, off-lattice theory of the equilibrium structure of dense polymer liquids is further developed in regard to the treatment of intramolecular polymer structure. A general scheme for self-consistently calculating the intramolecular and intermolecular pair correlations is outlined, along with the implementation of the integral equation theory for arbitrary ideal polymer models. A simple mathematical procedure for rigorously removing all unphysical intramolecular nonbonded monomer overlap is formulated in general and implemented for the freely jointed chain. The influence of the constant bond length and nonoverlapping constraints on the single-chain structure factor is studied numerically and discussed in the context of recent small-angle neutron-scattering experiments. An extensive series of model calculations of the intermolecular radial distribution function are performed for athermal polymer melts composed of Gaussian chains, Gaussian rings, and ideal and nonoverlapping freely jointed chains. The detailed dependence of both the local, short-range order and the correlation hole on degree of polymerization, density, and intramolecular flexibility is established, along with the limiting behavior for infinite molecular weight.

I. Introduction

The first tractable, microscopic, statistical mechanical theory for the equilibrium structure of dense one-component polymer melts in continuous space has been recently proposed by the present authors.[1-3] The approach employs an interaction site model of polymer structure and utilizes the integral equation theory of Chandler and Andersen[4,5] developed for small molecule fluids (the so-called "reference interaction site model" or RISM) to compute intermolecular site–site pair correlation functions. The high polymer problem is rendered mathematically tractable by exploiting the near ideality of polymers in the melt[1,2,6-8] and the relative unimportance of chain end effects for long linear macromolecules.[3] The resultant theory is computationally convenient and provides a quantitative description of both long- and short-range order and density fluctuations in dense polymeric liquids. The latter features distinguish our theory from the incompressible random-phase approximation (RPA) approach of deGennes,[6] which addresses only long-range correlations (small wave vector limit) of *labeled* species in the melt. The structural theory can also be employed to calculate thermodynamic properties of the polymer fluid. In principle, our integral equation theory is applicable for arbitrary models of single polymer configurational statistics and short-range intermolecular forces. However, published applications to date[1-3] have focused entirely on Gaussian chains and rings interacting via hard-core repulsions.

The development of a reliable theory of structure and wave vector dependent density fluctuations in polymer melts has many applications to important physical phenomena such as X-ray scattering, neutron scattering, and first-order phase transitions. In addition, the structure and thermodynamics of polymer blends appear to be sensitive to local correlations and compositional fluctuations as recently explicitly demonstrated via computer simulation.[9] A realistic treatment of short-range order in the isotropic liquid requires that some degree of the chemical structure of polymer molecules must be incorporated. In particular, a description of intramolecular structure beyond the

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