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Specific Solvent Effects in Swollen Polymer Networks

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ABSTRACT: Stress-strain isotherms at 25° have been determined for uniaxially elongated poly(dimethylsiloxane) networks in the unswollen state and swollen consecutively with each of the following very dissimilar diluents: low molecular weight dimethylsiloxane fluid, *n*-hexadecane, 2,4-dichlorotoluene, and *n*-octyl acetate. Five constant composition experiments were carried out, at values of the volume fraction v_2 of polymer of 1.00, 0.80, 0.60, 0.50, and 0.35. At $v_2 = 0.80$, the stress-strain isotherms were found to be independent of the nature of the diluent; at lower values of v_2, however, these isotherms were significantly different, thus demonstrating the existence of a "specific solvent effect" in swollen polymer networks. Interpretation of these data in terms of the statistical theory of rubber-like elasticity gave results in good agreement with previously reported specific solvent effects on the unperturbed dimensions of uncross-linked poly(dimethylsiloxane) chains in solution. In neither case, however, do these effects correlate well with the cohesive energy density or dielectric constant of the diluent or solvent medium.

In the study of the relationship between stress and strain in elongated polymer networks, measurements on samples containing diluent are usually more highly regarded than those carried out on unswollen specimens.[1-3] The primary reason for this preference is the observation[1-5] that stress-strain isotherms on swollen networks much more closely approach the form predicted by the theory of rubberlike elasticity.[1-3,6-8] An additional, and possibly related advantage is the relative rapidity with which swollen networks appear to reach elastic equilibrium.[9-13] Such diluents in swollen polymer networks have been treated customarily as entirely inert media in that their presence has been accounted for by simple geometric modification of the elastic equation of state to account for the reduction in the number of chains passing through unit cross-sectional area and the deformation of these chains to the new, increased volume of the swollen network.[1,2] According to the most general form[6-8] of the statistical or kinetic-molecular theory of rubberlike elasticity, however, the stress exhibited by a deformed polymer network depends on the unperturbed dimensions $\langle r^2\rangle_0$ of its constituent chains. As is now well known, $\langle r^2\rangle_0$ for a particular polymer of specified chain length generally depends on temperature because of differences in energy between various conformational states accessible to the chain backbone.[5,14,15] In addition, however, these dimensions are now known to depend at least in some cases on the *environment* of the chains.[16-24] Briefly, the unperturbed dimensions are obtained most reliably by viscometric or light-scattering measurements on the polymer chains at the Θ point, at which the chain co-volume is effectively zero and perturbations due to excluded volume are absent.[1] Although in such studies $\langle r^2\rangle_0$ is found to be at least approximately independent of the nature of the solvent medium in the case on nonpolar polymers, sizable differences are frequently observed in the case of significantly polar chains.[16-26] These differences, known loosely as "specific solvent effects," are thought to originate in solvent-induced changes in conformational energy, and thus in configuration and size, of the polymer chains. Such changes could arise from the dependence of intramolecular electrostatic interactions on the dielectric constant of the medium,[27-29] or from a less well understood direct interaction between solvent molecules and polymer chain segments.[22,30-32]

In any case, the demonstration[16-26] of a specific solvent effect on $\langle r^2\rangle_0$ from measurements on polymer solutions, and the presence of $\langle r^2\rangle_0$ in the theoretical elastic equation of state indicates that specific solvent (diluent) effects should also occur in appropriately chosen swollen polymer networks, with a discernible effect on stress-strain relationships at constant temperature. Unfortunately, there are relatively little data in the literature for testing this prediction; the only relevant studies pertain to networks prepared from natural rubber[10,11] and from polyethylene,[30] swollen, as required for comparison, with each of a number of diluents. In these cases, significant specific solvent effects were not observed but these results are not at all conclusive with regard to the possible existence of such an effect since the polymers employed are essentially nonpolar and there is probably considerable uncertainty in some of the results obtained using diluents of rather high volatility.

The purpose of the present study was therefore to determine stress-strain relationships at constant temperature for polymer network-diluent systems in which there would be maximum likelihood of observing specific solvent effects, if present. Networks prepared from poly(dimethylsiloxane) (PDMS) $(CH_3)_3Si[OSi(CH_3)_2]_xOSi(CH_3)_3$ were chosen as the best candidates for the following reasons. (i) PDMS chains are significantly polar,[28,29] and the unusual values obtained for the equation-of-state parameters of the polymer[33] and the thermodynamic properties of its solutions[34] suggest that polymer-diluent interactions might be particularly prominent in swollen PDMS networks; (ii) the wide-ranging solubility of the uncross-linked polymer[35] indicates that a variety of chemically dissimilar solvents would be suitable as network diluents; (iii) the polymer is easily cross-linked into networks which are readily extensible at room temperature and have excellent stability over extended periods of time,[36] and finally, (iv) the approximate magnitude of the specific solvent effect to be expected in swollen PDMS networks can be estimated from a summary[19] of reported values of $\langle r^2\rangle_0$ for PDMS chains in a variety of Θ solvents, in particular from values obtained from light-scattering intensities of PDMS chains in two chemically very different Θ solvents, at approximately the same temperature.[19]

Theory

The most general version[6-8] of the statistical theory of rubberlike elasticity characterizes the uniaxial elongation of a polymer network swollen to a volume fraction v_2 of polymer by

$$f^* v_2^{1/3}/(\alpha - \alpha^{-2}) = (\nu kT/V^*)[\langle r^2\rangle_i/\langle r^2\rangle_0] \tag{1}$$

where f^* is the force or stress divided by the cross-sectional area A^* of unswollen, undistorted network of volume V^*, and the strain is specified by the elongation α, which is the ratio of the length L of the elongated sample to its undistorted length L_i at the swollen volume V prevailing at the specified pressure, temperature T, and force f. The quantity $f^* v_2^{1/3}/(\alpha - \alpha^{-2})$ constituting the left-hand side of this elastic equation of state is frequently referred to as the "modulus" or "reduced force" of the network. The quantity ν is the number of chains in the network and k is the Boltzmann constant; $\langle r^2\rangle_i$ is the mean-square end-to-end distance for a network chain in the undistorted state of volume V^* (and thus is independent of v_2), and $\langle r^2\rangle_0$ (the "unperturbed dimensions") is the corresponding quantity for the free chain in the absence of the network cross-links. Thus, according to theory, at constant temperature and volume fraction of polymer, the modulus of a swollen polymer network should vary inversely with the unperturbed dimensions of its constituent chains in the solvent being employed as diluent.

This expected inverse proportionality between modulus and $\langle r^2\rangle_0$ may, however, be complicated by the fact that stress-elongation results frequently depart[37-39] from the form given in eq 1 in that the modulus varies with α according to[40]

$$f^* v_2^{1/3}/(\alpha - \alpha^{-2}) = 2C_1 + 2C_2\alpha^{-1} \tag{2}$$

$2C_1$ and $2C_2$ being constants the identification and origin of which are issues still to be resolved. Comparison of eq 1 and 2 shows that the term $2C_2\alpha^{-1}$ serves as an empirical correction to the theoretical equation of state. In attempting to investigate possible specific solvent effects in swollen networks, it will therefore be necessary to consider the effects of diluent on $2C_1$ and $2C_2$, as well as on the modulus $f^* v_2^{1/3}/(\alpha - \alpha^{-2})$.

Experimental Section

Materials. The polymer used in the preparation of the networks was an unfractionated sample[41] of PDMS having a molecular weight of approximately 1.4×10^6. On the basis of a number of preliminary swelling experiments, the following solvents were chosen for use as network diluents: dimethylsiloxane fluid (DMS) of degree of polymerization $\sim 10^2$, *n*-hexadecane (nHD), 2,4-dichlorotoluene (DCT), and *n*-octyl acetate (nOA), the last three of these being of "reagent-grade" purity. As is readily evident, there is considerable variation in chemical structure in this series of solvents. All are good swelling agents for PDMS networks and all have boiling points above 200°, thus making negligible the possible loss of solvent from the swollen networks in the vicinity of room temperature. The specific volumes of these solvents at 25°, as measured by pycnometry, are: DMS, 1.035; nHD, 1.300; DCT, 0.8040; and nOA, 1.157 cm^3 g^{-1}. The similarly measured value[42] for PDMS at the same temperature is 1.031 cm^3 g^{-1}.

Preparation of Networks. A series of networks had previously been prepared from this particular sample of PDMS and the cross-linking conditions which were employed are described in detail in a previous study[36] of the properties of a number of these networks. In brief, sheets of the polymer approximately 0.1 cm thick had been irradiated with high-energy electrons, in an atmosphere of nitrogen at room temperature. Of the series of samples which had been thus prepared,[36] two were chosen for the present experiment; since relatively high degrees of swelling were desired, these two networks had the relatively low radiation doses of 4 and 2 Mrads, respectively. Preliminary swelling equilibrium measurements at 25°, using the diluents described in the preceding section, indicated that the first of these networks was of only moderately high degree of cross-linking and the second was even more lightly cross-linked.

A dumbbell-shaped sample was die-pressed from each of these two cross-linked sheets. In order to extract soluble (uncross-linked) polymer from these samples, both were placed in gently stirred *n*-hexane for a period of 3 days, during which time two very thin copper wires were inserted into the middle portion of each of them. The samples were then deswollen in methanol, and dried under vacuum to constant weight. This procedure, carried out entirely at room temperature, resulted in the extraction of 7 and 27 wt % soluble material from the 4- and 2-Mrad samples, respectively. The sample test sections, located between the wire reference markers, were of uniform cross-section and had dimensions of approximately 0.1 × 0.6 × 3.0 cm in the unswollen state. The precise values of the cross-sectional area A^* of the undistorted unswollen networks at 25° were determined using both a cathetometer and micrometer.

Stress-Elongation Measurements. Stress-strain isotherms at 25° were determined for these networks, both swollen and unswollen, in uniaxial elongation exactly as has been described previously.[39,42,43] In brief, the elongation was obtained from the distorted and undistorted lengths of the sample test section, which were measured by means of a cathetometer. The corresponding stress was recorded using the same transducer-recorder assembly employed in several previous studies.[39,42,43] Four or five elongations in the range α = 1.1-1.8 were used in the determination of each isotherm and measurements were made using both increasing and decreasing series of elongations, in order to test for reversibility.

The more highly cross-linked network (4Mrads) was studied first. After its stress-strain isotherm in the unswollen state was determined for reference purposes as already described, the network was swollen to the desired value of v_2 by placing it in contact with small amounts of DMS that had been purged with nitrogen in order to remove any dissolved oxygen. DMS was thus added until the weight absorbed by the network corresponded to that giving the desired value of v_2, 0.80, calculated on the assumption of additivity of volumes of polymer network and diluent. (In general, deviations from this assumed additivity of volumes in polymer-solvent systems seldom exceed a few per cent in magnitude.[44,45] They are further reduced in importance in the present circumstance by the dependence of the modulus on only the cube root of v_2, if possible specific solvent effects are temporarily neglected; see eq 1.) After sufficient time had elapsed to assure uniformity of swelling, the stress-strain isotherm of the swollen network was measured. The network was then deswollen and dried as already described, and its stress-strain isotherm in the unswollen state redetermined in order to check for possible network degradation. The above procedures were then carried out for this network using each of the remaining three diluents at v_2 = 0.80, and then for each of the four diluents at v_2 = 0.60. Lower values of v_2 required use of the less highly cross-linked network (2 Mrads). Stress-strain isotherms were therefore determined in exactly the same manner for this network in the unswollen state, and swollen to values of v_2 = 0.50 and 0.35. In no case did the actual adjusted value of v_2 of a swollen network differ from the values cited above by more than ±0.0025 unit, and in no case was there any evidence of loss of diluent during the stress-elongation measurements.

It is important to note that the desired comparison of stress-strain isotherms obtained using different diluents is considerably simplified by the present scheme in which a single sample is used to obtain a complete set of results at each specified degree of dilution.

Results and Discussion

Good agreement was found between stress-strain data obtained using increasing and decreasing series of values of the elongation, thus indicating that the techniques described in the preceding section gave results of the required reproducibility. Similarly, good reproducibility was observed for results obtained on the unswollen network before and after measurements in the swollen state, thus demonstrating the absence of network degradation.

The modulus $f^* v_2^{1/3}/(\alpha - \alpha^{-2})$ at 25° was plotted

Table I
PDMS Network Characteristics and Stress-Elongation Results at 25°

Radiation Dose (Mrads)	v_2	Diluent	$f^*v_2^{1/3}/(\alpha - \alpha^{-2})^a$	$2C_2{}^b$	$2C_1{}^b$	$\frac{\langle r^2\rangle_0}{\langle r^2\rangle_0\text{DMS}}$
4	1.00		1.058	0.81	0.448	
	0.80	DMS	0.902	0.64	0.408	1.00
		nHD	0.890	0.62	0.416	0.98
		nOA	0.891	0.64	0.398	1.03
	0.60	DMS	0.795	0.53	0.390	1.00
		nHD	0.770	0.45	0.420	0.93
		nOA	0.747	0.37	0.466	0.84
2	1.00		0.651	0.74	0.0860	
	0.50	DMS	0.177	0.15	0.0626	1.00
		nHD	0.162	0.12	0.0715	0.88
		nOA	0.156	0.093	0.0845	0.74
	0.35	DMS	0.116	0.073	0.0591	1.00
		nHD	0.112	0.059	0.0667	0.89
		nOA	0.104	0.029	0.0818	0.72

[a] Kg cm^{-2} at α = 1.300. [b] kg cm^{-2}.

against the reciprocal of the elongation α, as suggested by eq 2, and least-squares analysis was used to locate the best straight line representing each such stress-strain isotherm. The results for the 4-Mrad sample in the swollen state are shown in Figure 1, and the corresponding results for the 2-Mrad sample are shown in Figure 2. A summary of the results is given in Table I, where values of modulus at α = 1.300, the slope $2C_2$ and the intercept $2C_1$ are given for each isotherm, including those for the undiluted networks. Stress-elongation isotherms for the 4-Mrad sample swollen with nHD and with DCT were essentially identical at both v_2 = 0.80 and 0.60; these results for DCT were therefore not included in Figure 1 and Table I, and this solvent was not used as a diluent for the 2-Mrad sample.

It is perhaps appropriate to begin analysis of these results by noting that in all cases the $2C_2$ factor in the correction term of eq 2 is seen to decrease with decreasing degree of cross-linking and with decreasing v_2, in agreement with results[36] previously obtained on swollen and unswollen PDMS networks. The results obtained on the 4-Mrad sample at v_2 = 0.80 were essentially identical for all three diluents (DMS, nHD, nOA) and, as can be seen in Figure 1, the least-squares line drawn through the results obtained using DMS as diluent satisfactorily represents those obtained using the other two diluents as well. (This uniformity of behavior is, of course, to be expected when only relatively small amounts of diluent are present in the swollen network.) As shown in Figures 1 and 2, however, significant differences in the stress-elongation isotherms do appear at v_2 = 0.60 in the case of the 4-Mrad sample, and at v_2 = 0.50 and 0.35 in the case of the 2-Mrad sample. The fractional change in the modulus with change in diluent at constant v_2 seems in general to be largest in the case of small v_2, as would be expected from the decreasing effect of polymer-polymer interactions as increasing amounts of diluent are incorporated into the network.

As shown in Table I, when interest is focused on a single diluent, values of $f^*v_2^{1/3}/(\alpha - \alpha^{-2})$ at α = 1.300 nevertheless vary considerably with v_2, in disagreement with the theoretical relationship given in eq 1. This variation of the modulus with v_2, and also with α itself, has led some workers to identify the right-hand side of eq 1 with $2C_1$,[46] the value of $f^*v_2^{1/3}/(\alpha - \alpha^{-2})$ at α^{-1} = 0, where the correction term containing $2C_2$ in eq 2 vanishes. Since the origin of the $2C_2$ correction is not understood at present, such analysis of stress-strain data is necessarily very tentative.[46] In any case, values of $2C_1$ thus obtained generally[46] show only a relatively slight dependence on v_2; in the present study they vary by 5% over the range v_2 = 1.00–0.60 in the case of the 4-Mrad sample and by 13% over the range 1.00–0.35 in the case of the 2-Mrad sample. We thus tentatively identify $2C_1$ with the quantity $(\nu kT/L_iA^*)[\langle r^2\rangle_i/\langle r^2\rangle_0]$ of eq 1, thus permitting calculation of the ratio of values of $\langle r^2\rangle_0$ for the network chains in two diluents at the same value of v_2. For convenience, the reference diluent arbitrarily chosen for the calculation of these ratios was DMS, which is, of course, virtually identical to the PDMS chains of the swollen network. Values of the desired ratio $\langle r^2\rangle_0/\langle r^2\rangle_0$(DMS) are listed in the last column of Table I, and unambiguously demonstrate the existence of a specific solvent effect in swollen PDMS networks. In the pertinent concentration range v_2 = 0.60–0.35, the ratio invariably decreases in the order DMS, nHD, nOA; the magnitude of this specific solvent effect is well beyond the experimental error in the measurements, and, in general, increases with decrease in v_2, as expected. The results pertaining to the highest dilution, v_2 = 0.35, should be the ones most directly comparable to the specific solvent effects observed for solutions of (uncross-linked) PDMS at infinite dilution.[19] The maximum difference ob-

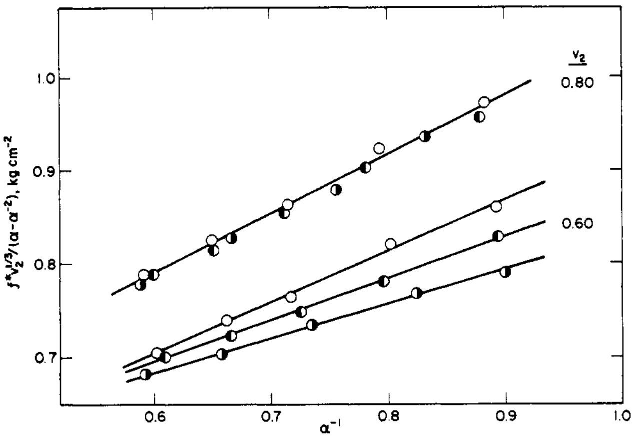

Figure 1. The modulus or reduced force *vs.* the reciprocal of the elongation for the PDMS network of moderately high degree of cross-linking (4 Mrads), at 25°. The values of v_2 shown specify the volume fraction of polymer in the swollen network. The open, left-filled, and right-filled circles locate results obtained using the diluents dimethylsiloxane fluid, *n*-hexadecane, and *n*-octyl acetate, respectively.

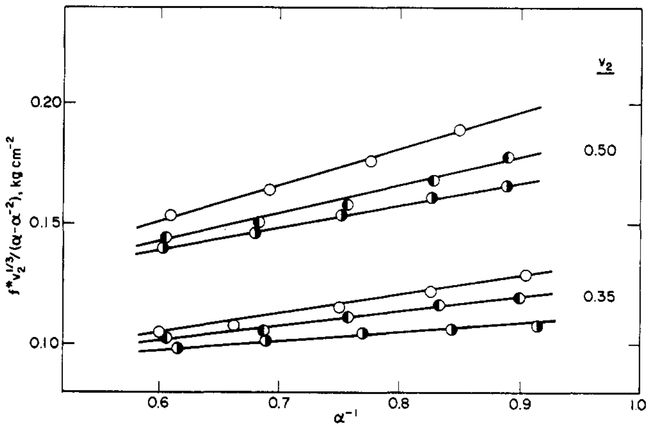

Figure 2. The modulus *vs.* reciprocal elongation for the lightly cross-linked PDMS network (2 Mrads); see legend to preceding figure.

served for PDMS network chains at this value of v_2 amounts to 28%. This result is in excellent agreement with the maximum difference of 24% found among the eleven reported values[19] of the unperturbed dimensions of uncross-linked PDMS chains in eight Θ solvents in the temperature range 2-90°. It is also interesting to note that dielectric constant measurements on uncross-linked PDMS chains in cyclohexane and in the undiluted state at a variety of temperatures yield values of the mean-square dipole moment $\langle\mu^2\rangle_0$ which also differ by approximately 20% in the vicinity of 25°.[29]

Of the various studies carried out on uncross-linked PDMS chains in Θ solvents,[19] the most interesting is a report of light-scattering measurements on PDMS in two Θ solvents, specifically methyl ethyl ketone and the mixed solvent C_8F_{18} + CCl_2FCCl_2F, at almost exactly the same temperature.[19] These two solvents are of very different cohesive energy density (ced), which is the energy of vaporization per unit volume and is thus a measure of the intermolecular forces in the liquid thus characterized. The values of $\langle r^2\rangle_0$ for PDMS in these two solvents differed by approximately 18%. Furthermore, the mixed solvent system is particularly interesting in that its ced (46 cal/cm^3)[19] is even lower than the unusually small value (53 cal/cm^3)[19,47] characterizing PDMS itself. The value of $\langle r^2\rangle_0$ obtained in this Θ solvent is substantially larger than that obtained in any other of the Θ solvents, all of which have values of the ced larger than that of PDMS.[19] The specific solvent effects found in the present study are in agreement with this observation in that $\langle r^2\rangle_0$ of the network chains is also largest in DMS, which has a value of (~53 cal/cm^3)[48] of the ced that is significantly lower than any of the values of the other diluents studied.

The entire collection of results on PDMS chains in solution and in the swollen networks do not, in general, show a correlation of $\langle r^2\rangle_0$ with either ced or dielectric constant of the medium. The same appears to be true for other polymer chains as well.[16-18,20-26] The origin of this specific solvent effect is thus still ambiguous and there is obviously a need for additional reliable data in this area, particularly in the case of polymers of high polarity.

On the practical side, it appears from the present results that, although incorporating diluent into a polymer network may hasten the attainment of elastic equilibrium and minimize $2C_2$ deviations from the theoretical elastic equation of state, new uncertainties in interpretation may arise. At least in the case of polar polymers, specific solvent interactions may affect significantly the unperturbed dimensions of the network chains and thus also the modulus of the polymer network.

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