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Model Networks of End-Linked Polydimethylsiloxane Chains. 5. Dependence of the Elastomeric Properties on the Functionality of the Network Junctions

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Abstract: Elastomeric networks of carefully controlled structure were prepared by end-linking hydroxyl-terminated polydimethylsiloxane chains of known molecular weight by means of a trialkoxysilane $(C_2H_5O)_3RSi$. The reactions were carried out both in the undiluted state and in solution, in order to assure stoichiometric completeness in the formation of the network structures. The trifunctional networks thus prepared were studied with regard to their stress–strain isotherms in the unswollen state, in elongation at 25 °C, and with regard to their equilibrium swelling in benzene at room temperature. Values of the modulus in the limits of large and small deformations were found to be in satisfactory agreement with theoretical predictions for nonaffine and affine deformations, respectively (the latter corresponding to the case in which the displacements of the network chain vectors are a simple linear function of the macroscopic strain). Comparisons with results previously obtained on the corresponding tetrafunctional networks showed that both of these moduli have very nearly the expected dependence on network functionality. The equilibrium swelling data were interpreted to estimate the extent to which the swelling deformation approaches the affine limit. The results for both the trifunctional and tetrafunctional networks are in very good agreement with a recent theory of network swelling in which the closeness of the approach to the affine limit depends on both the network structure and the degree of swelling.

Introduction

One of the most striking properties of flexible polymer chains is the rubberlike elasticity they exhibit when cross-linked into network structures.[1,2] Although this unique type of elastic behavior has been under investigation for over a century now, there are still a number of important unresolved issues in this area. The most important of these concerns the relationships between the equilibrium elastomeric properties of a polymer network and the details of its molecular structure. Relatively little has been accomplished in definitively establishing such relationships because of serious difficulties in obtaining independent information on the network structure. The method of preparation of the network seldom provides information in this regard because of the highly random, uncontrolled manner in which the cross-links are usually introduced.[1,2]

It is now possible, however, to prepare "model" networks in which important characteristics of the network structure are known and controllable, because of the selectivity of the cross-linking reaction. One of the most useful chemical reactions of this type involves linking the chains exclusively through functional groups placed at their two ends.[3-9] The crucially important molecular weight M_c between cross-links is then simply the (known) molecular weight of the chains prior to their incorporation into the network structure. Furthermore, with this technique it is also possible to vary the functionality ϕ of a network cross-link (the number of chains emanating from it) by suitable choice of end-linking reactant.

The present study involves the preparation of end-linked polydimethylsiloxane (PDMS) networks having known network chain length, and a known cross-link functionality of three, instead of the usual functionality of four. The networks are characterized with regard to their stress–strain isotherms in elongation and their degree of equilibrium swelling in a thermodynamically good solvent. The results are used to establish the relationship between the modulus of a network and its degree of cross-linking or, equivalently, the molecular weight M_c of its network chains. The equilibrium swelling data are employed primarily to estimate the extent to which the swelling deformation approaches the affine limit, in which the molecular dimensions are assumed to vary linearly with the changes in the macroscopic dimensions of the elastomeric sample. Comparisons with previously published results on the corresponding tetrafunctional PDMS networks are then used to elucidate the effect of cross-link functionality on the elastomeric properties of polymer networks.

Experimental Section

The polymer used was an unfractionated sample[3,5,7,8,10] of PDMS having hydroxyl groups at both ends, a number-average molecular

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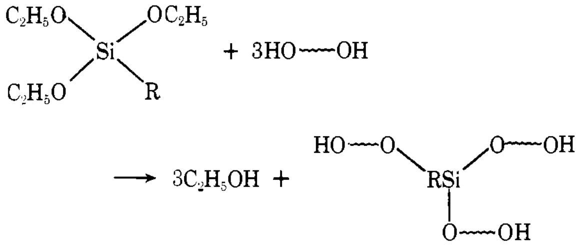
Table I. Conditions of Preparation, Elastomeric Properties, and Structural Characteristics of the PDMS Networks

					elongation				swelling	
$10^{-3}M_n$, g mol^{-1}	diluent present during cross-linking	v_{2S}[a]	v_{2C}[b]	$\bar{v}_{2C}$[c]	$2C_1$, N mm^{-2}	$2C_2$, N mm^{-2}	A_3	A_3'	v_{2m}[d]	F_3[e]
18.5	P[f]	1.00	0.944	0.944	0.0902	0.0760	0.72	1.33	0.228	0.62
					0.0949	0.0715	0.76	1.33	0.227	0.61
	C[g]	0.90	0.858	0.886	0.0661	0.0676	0.55	1.11	0.202	0.46
					0.0728	0.0731	0.61	1.22	0.220	0.58
		0.80	0.718	0.781	0.0566	0.0465	0.51	0.94	0.182	0.39
					0.0501	0.0410	0.45	0.83	0.182	0.39
		0.70	0.649	0.741	0.0676	0.0762	0.64	1.35	0.205	0.54
					0.0638	0.0582	0.60	1.15	0.200	0.51
					0.0637	0.0699	0.60	1.25	0.201	0.52
	L[h]	0.90	0.828	0.833	0.0741	0.0587	0.64	1.15	0.209	0.53
					0.0747	0.0634	0.65	1.20	0.207	0.52
		0.90	0.820	0.826	0.0612	0.0525	0.53	0.99	0.190	0.41
					0.0558	0.0546	0.49	0.96	0.189	0.42
		0.80	0.749	0.756	0.0692	0.0590	0.64	1.19	0.198	0.50
					0.0613	0.0654	0.57	1.17	0.192	0.46
		0.70	0.650	0.660	0.0484	0.0525	0.49	1.02	0.174	0.39
					0.0499	0.0526	0.51	1.04	0.176	0.40
18.5[i]	P	1.00	0.970	0.970	0.0660	0.0606	0.52	0.99	0.203	0.44
32.9[i]	P	1.00	0.970	0.970	0.0342	0.0327	0.48	0.93	0.170	0.51
25.6[i]	P	1.00	0.971	0.971	0.0440	0.0507	0.48	1.03	0.184	0.47
9.5[i]	P	1.00	0.989	0.989	0.0918	0.0578	0.36	0.60	0.274	0.53
4.7[i]	P	1.00	0.970	0.970	0.146	0.0110	0.29	0.31	0.301	0.35
4.0[i]	P	1.00	0.979	0.979	0.189	0.0182	0.32	0.35	0.300	0.29

[a] Volume fraction of polymer in the system being cross-linked. [b] Volume fraction of polymer successfully incorporated into the network structure. [c] Volume fraction v_{2C} corrected for volatility losses of diluent during cross-linking. [d] Volume fraction of polymer in the network at swelling equilibrium in benzene at room temperature. [e] A measure of the extent to which the deformation approaches the affine limit. [f] No diluent other than soluble (uncross-linked) polymer. [g] Cyclic dimethylsiloxane oligomer. [h] Linear dimethylsiloxane oligomer. [i] Reference 7.

weight M_n of 18.5×10^3 g mol^{-1}, and a polydispersity index of 1.87. The reaction used to end link these chains was



(1)

in which HO∿∿OH represents the hydroxyl-terminated PDMS chains. The specific end-linking agent employed was triethoxyvinylsilane, since the vinyl group is unreactive under the end-linking conditions employed. The catalyst employed was tin(II) 2-ethylhexanoate, and was present to approximately 0.6% by weight of the polymer. In order to assure stoichiometric completeness in the formation of the network structures, the reactions were carried out both in the undiluted state and in solution. The diluents were cyclic dimethylsiloxane oligomer (C) and linear dimethylsiloxane oligomer (L);[10] they were chosen in part because of their relatively low volatilities. (The number-average degrees of polymerization of the C and L oligomers were 5 and 9, respectively.) The catalyst and diluent were stirred directly into the liquid-like PDMS. After the mixture appeared homogeneous, the stoichiometrically required amount of the trifunctional cross-linking agent was added, and also incorporated by stirring. The values of the volume fraction v_{2S} of polymer in the mixtures thus prepared were 0.90, 0.80, and 0.70. (In one case, neither of the two diluents was added (v_{2S} = 1.00), in order to check the previously published results[7] on PDMS networks thus prepared. In this reaction, the only "diluent" present was therefore the (soluble) polymer (P) that did not become incorporated into the network structure.)

The mixtures of ingredients were poured into aluminum molds and the reaction was allowed to proceed at room temperature for 2 days, as was described previously.[3] The reaction was carried out under vacuum, in order to remove the ethanol byproduct, and this of course also removed some of the diluent employed. Over the 2-day period, approximately 60% of the C and 12% of the L diluents were removed.

The networks thus prepared were extracted and dried as described elsewhere.[3] The amount of soluble (uncross-linked) material removed was approximately 6% of the total weight of polymer. The exact amount of soluble material was used to correct v_{2S} to v_{2C}, the volume fraction of polymer successfully incorporated into the network structure; these values are given in column 4 of Table I. They were further corrected for the volatility losses of diluent mentioned above, in order to yield the average value $\bar{v}_{2C}$ during the end-linking procedure. The results are given in the following column of the table.

The stress-strain isotherms were obtained on strips cut from the dried (unswollen) networks, at 25 °C, in the usual manner.[3,7,11,12] Stress-strain measurements were made using a sequence of increasing values of the elongation or relative length of the sample $\alpha = L/L_i$, with frequent inclusions of values out of sequence to test for reversibility. Entire stress-strain isotherms were generally repeated two or three times. In some cases, an entirely new network was prepared, and these duplicate runs thus served as tests primarily of the reproducibility of the synthetic techniques employed. In other cases, different strips were cut from the same network sheet, thus providing a test primarily of the stress-strain measuring techniques.

Equilibrium swelling measurements were carried out on each of the network strips, in benzene at room temperature, as described previously.[3] The extent of swelling was characterized by v_{2m}, the volume fraction of polymer at maximal swelling, which was calculated assuming simple additivity of volumes.

Results and Discussion

The stress-strain data were interpreted in terms of the "reduced stress" or modulus defined by[3,11-14]

$$[f^*] \equiv f/[A^*(\alpha - \alpha^{-2})] \qquad (2)$$

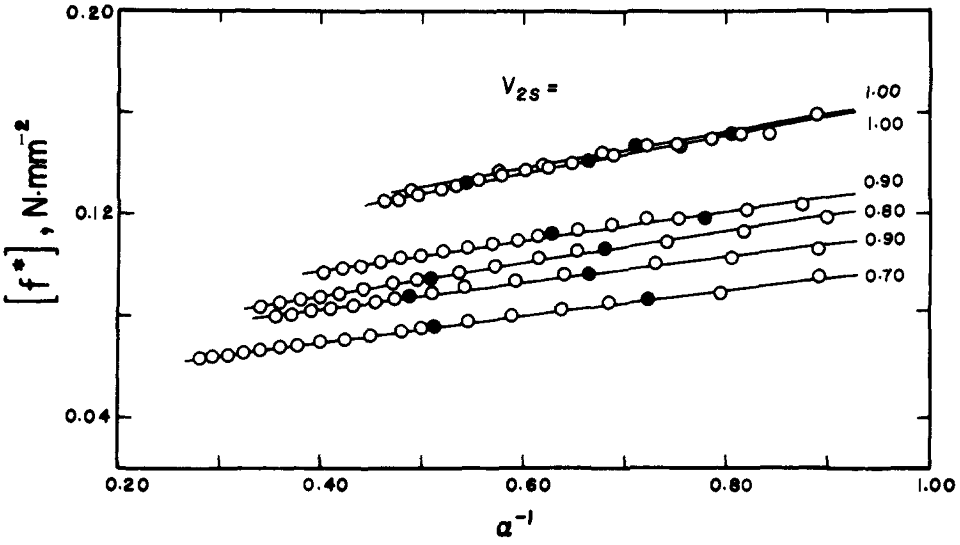


Figure 1. Typical stress-strain isotherms, in elongation at 25 °C, for the PDMS networks prepared in the undiluted state and in solution with the linear dimethylsiloxane oligomer as diluent. Each curve is identified by the value of the volume fraction v_{2S} of polymer present during the end-linking process. Results gotten using a series of increasing values of the elongation α are located by the open circles; the other results, shown by the filled circles, were obtained using values of α out of sequence in order to test for reversibility. All isotherms were located by least-squares analysis. The duplicate isotherms shown for v_{2S} = 1.00 were obtained using the same network and thus illustrate the reproducibility of the stress-strain measurements. The duplicate isotherms at v_{2S} = 0.90 were obtained on different networks and thus illustrate the reproducibility of the synthetic techniques employed.

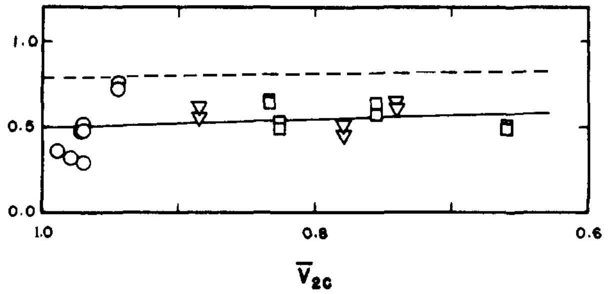


Figure 2. Experimental values of the structure factor A_3 obtained from the high elongation limit $2C_1$ of the elongation modulus, shown as a function of the volume fraction of polymer successfully incorporated into the network structure. The diluents present during the end-linking process were (1) only the polymer which did not become incorporated into the cross-linked network (○), (2) cyclic dimethylsiloxane oligomer (▽), and (3) linear dimethylsiloxane oligomer (□). The solid line represents the present results, on the trifunctional networks, and the broken line the corresponding results[8] on the tetrafunctional networks. Both lines were located by least-squares analysis.

where f is the equilibrium value of the elastic force and A^* is the cross-sectional area of the undeformed sample. The values of $[f^*]$ were plotted against reciprocal elongation, as suggested by the semiempirical equation of Mooney and Rivlin:[15]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \quad (3)$$

in which $2C_1$ and $2C_2$ are constants independent of α. Thus the value of the modulus is $2C_1$ in the limit at large deformation ($\alpha^{-1} \rightarrow 0$), and $2C_1 + 2C_2$ in the limit at small deformation ($\alpha^{-1} \rightarrow 1$). Typical stress-strain isotherms, thus represented, are shown in Figure 1. Least-squares analysis was used to locate the best lines through these and the other isotherms. The results obtained upon decreasing α are seen to be in excellent agreement with those obtained during the main sequence of increasing value of α, thus demonstrating the reversibility of the isotherms. The values of the constants $2C_1$ and $2C_2$ characterizing each isotherm are given in columns 6 and 7 of Table I. Included in the last six rows are the corresponding results[7] previously obtained on networks prepared by trifunctionally end-linking undiluted PDMS chains of various molecular weights. As can be seen from the figure and from the more extensive sets of values of $2C_1$ and $2C_2$ listed in Table I, there was a high degree of reproducibility in the end-linking techniques used to synthesize the networks, and in the techniques used to determine the equilibrium values of the stress and strain in the elongated networks.

The values of $2C_1$ listed in Table I were interpreted using the equation[8,16,17]

$$2C_1 = A_3\rho kT\bar{v}_{2C}^{2/3}M_n^{-1} \quad (4)$$

in which A_3 is the "structure factor" for the trifunctional network, ρ is the density of the network, k is the Boltzmann constant, and T = 298.2 K is the absolute temperature. The factor $\bar{v}_{2C}^{2/3}$ takes into account the fact that drying a solution-cross-linked network has a compressive effect on the dimensions of the network chains, with corresponding decreases in the observed values of $[f^*]$ and $2C_1$.[12,18,19] The average molecular weight M_c between cross-links in the network (i.e., the molecular weight of the network chains) has been taken to be M_n of the PDMS chains prior to their cross-linking, because of the nature and near completeness of the end-linking reaction.[3,4] Since $2C_1$ represents the modulus in the limit of large elongation, the deformation should be nonaffine, approximating that of a phantom network, in which the mean positions of the junctions deform affinely, but the junction fluctuations are invariant.[3,16,17,20] The value of A_ϕ for such a nonaffine deformation of a ϕ functional network is given by $1 - 2/\phi$, and should therefore be $1/3$ for the present trifunctional case.[16,17,21,22] The values of A_3 thus calculated are given in column 8 of Table I and are plotted against $\bar{v}_{2C}$ in Figure 2. The line shown in this figure, and the ones shown in the following two related figures, were all located by least-squares analysis. The values of A_3 show no trend whatever with decrease in $\bar{v}_{2C}$, which argues strongly that the end-linking reaction is very nearly complete even in the absence of diluent.

In a study of this type, it is of particular importance to demonstrate that the end-linking reaction does go essentially to completion. The additional evidence bearing on this point is therefore summarized here since the amount of extractable material observed in these networks might otherwise be misinterpreted to suggest a lower extent of reaction. In fact, the

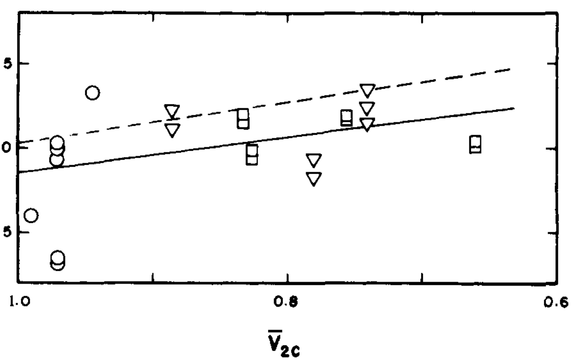


Figure 3. The structure factor A_3' obtained from the low elongation limit ($2C_1 + 2C_2$) of the elongation modulus. See legend to Figure 2.

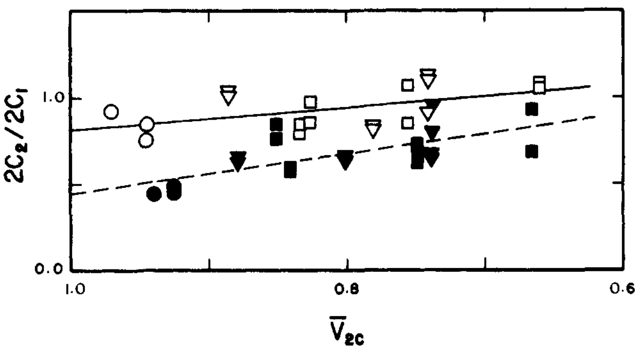


Figure 4. Values of the ratio of the Mooney–Rivlin constants characterizing the stress–strain isotherms. The present results on the trifunctional networks are located by the open symbols and the solid line; the corresponding results for the tetrafunctional networks are shown by the filled symbols and the broken line. See text and legend to Figure 2.

soluble portion of the cross-linked systems can be accounted for almost entirely by the 2–6% of inert dimethylsiloxane cyclics generally present in the polymer samples employed, according to chromatographic measurements.[23] Furthermore, the average value of 6% cited for the soluble material is generally artificially high because of the inclusion of unavoidable weight losses in removing the samples from the molds in which they were cross-linked. As expected, fractionation of the PDMS prior to its end-linking can reduce the soluble fraction significantly, to as low as 1%, without any discernible increase in the modulus of the resulting network.[7] Also of direct relevance are alkoxy group analyses showing ethoxy groups to be absent in the networks[3,7] and chain extension measurements[7,24] showing that simply heating such a hydroxyl-terminated PDMS sample under vacuum increases its molecular weight by more than an order of magnitude. It is also observed that increase in reaction time has very little effect on the resulting networks, chemically different cross-linking reactions give essentially equivalent results,[25] and the unusually large maximum extensibility of the end-linked networks[3,26] suggests that the number of dangling-end irregularities is unusually small. Finally, degradation studies[8,27] of PDMS networks give results in good agreement with those obtained in the present series of investigations.

The average value of A_3, 0.54 with a standard deviation of 0.11, is in satisfactory agreement with theory, considering the relatively long extrapolations required to obtain the experimental values of $2C_1$. The corresponding theoretical and experimental values of A_4 for the tetrafunctional networks are $\frac{1}{2}$ and 0.81 (±0.16), respectively.[8] The experimental value of the ratio A_3/A_4 characterizing the dependence of the high deformation modulus on cross-link functionality is thus 0.67; it is in essentially exact agreement with the theoretical value of $\frac{2}{3}$.[16,17,28]

It is also useful to interpret the modulus in the limit of small deformation since a much shorter extrapolation is required, and this is the quantity analyzed by Macosko[4,9] and Graessley[29] in some related experiments. One disadvantage is the fact that $2C_1 + 2C_2$ slightly overestimates this limiting value of the modulus because of the nonlinear leveling off of the modulus as the elongation decreases toward unity.[17,30,31] In any case, in this region the deformation should be very nearly affine, and the factor A_3' defined by

$$2C_1 + 2C_2 = A_3'\rho kT\bar{v}_{2C}^{2/3}M_n^{-1} \qquad (5)$$

should be equal to unity,[16,17,32] as it should be, in fact, for networks of any functionality. The observed values of A_3' are presented in column 9 of Table I, and are shown as a function of $\bar{v}_{2C}$ in Figure 3. The slight trend in A_3' with $\bar{v}_{2C}$ is probably not significant because of the relatively large amount of scatter in the results.[28] The average value of A_3' is 1.02 (±0.27), which is in excellent agreement with theory. The corresponding theoretical and experimental values of A_4' for the tetrafunctional networks are 1 and 1.29 (±0.36), respectively. The experimental value of the ratio A_3'/A_4' is thus 0.79, in reasonably good agreement with the predicted value of unity.

The separate constant $2C_2$ is also of considerable interest since it is a measure of the extent to which the elongation deformation changes from essentially affine to the phantom limit with increasing stress, and is therefore directly related to the looseness with which the cross-links are embedded in the network structure.[16,17,20] It should thus be larger for the trifunctional networks, since cross-links acting as junctions for three chains instead of four would be less constrained by chain-junction entanglements and thus less firmly embedded in the network medium. Quantitative evaluation of these experimental results is very difficult, however, since theory[17,31] indicates that the simple linearity expressed in eq 3 is valid for only a relatively small range in elongation. In any case, theory suggests that $(2C_2/2C_1)_3/(2C_2/2C_1)_4$ should be on the order of 2. Since $2C_2$ is known to depend on degree of cross-linking,[13] only the experimental results obtained at the constant value $M_c = 18.5 \times 10^3$ are pertinent, and these are presented in Figure 4. Simply averaging the results for the two types of networks gives a value of $(2C_2/2C_1)_3/(2C_2/2C_1)_4$ of 1.4, in fair agreement with the theoretical value of 2, considering the difficulty[13] in obtaining reliable values of $2C_2$. If attention is focused on the networks prepared in the absence of any diluent (which can complicate the comparison through its effect on the topology of the resulting networks),[16,33] then the experimental value of this ratio is 1.8, in excellent agreement with theory.

The values of the volume fraction v_{2m} of polymer in each of the networks at swelling equilibrium in benzene at room temperature are given in column 10 of Table I. The interpretation of the swelling results utilized the very recent theory of Flory,[19] in which the extent to which the deformation is nonaffine depends on the looseness with which the cross-links are embedded in the network structure. This depends in turn on both the structure of the network and its degree of equilibrium swelling. In this case, comparisons between theory and experiment are most conveniently carried out in terms of the equation[19]

$$M_c = -F_\phi \rho V_1 \bar{v}_{2C}^{2/3} v_{2m}^{1/3}/[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2] \qquad (6)$$

in which F_ϕ is a factor characterizing the extent to which the deformation in swelling approaches the affine limit, $V_1 = 89.08$ cm^3 mol^{-1} is the molar volume of the benzene, and χ_1 is the free energy of interaction parameter[1] between the benzene and the PDMS networks. The required values of χ_1 were obtained from published results,[14] which indicate $\chi_1 = 0.484 +$

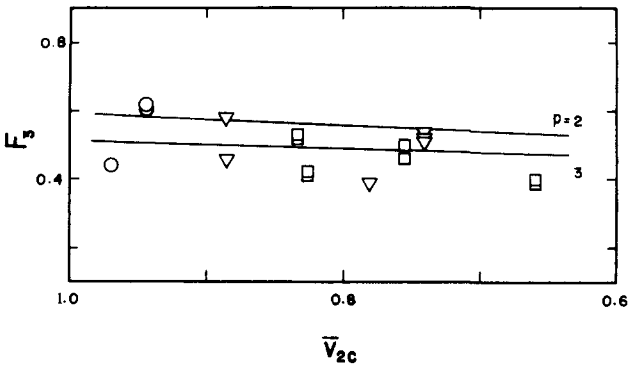


Figure 5. The factor characterizing the extent to which the deformation in swelling approaches the affine limit for the trifunctional networks. The lines shown are the values predicted using a theory[19] of swelling equilibrium in which the extent of nonaffineness depends on the network structure as well as its degree of swelling. The values of the parameter[19] characterizing the dependence of the cross-link fluctuations on the strain are specified for both of the theoretical lines.

$0.330v_{2m}$ for the pertinent range of v_{2m}. The values thus obtained ranged from 0.540 to 0.583.

The experimental values of the factor F_3 for all of the trifunctional networks having $M_c = 18.5 \times 10^3$ were calculated by inserting this molecular weight and the appropriate values of the other parameters into eq 6. The results are located by the points shown in Figure 5, and give the average value 0.48 ($\pm$0.07). The theoretical values of F_ϕ are given by[16,17,19]

$$F_\phi = (1 - 2/\phi)[1 + (\mu/\xi)K] \qquad (7)$$

where μ is the number of junctions, ξ is the cycle rank of the network, and K is a function of v_{2m}, and also of two network parameters κ and p which specify respectively the constraints on the cross-links from the neighboring chains and the dependence of the cross-link fluctuations on the strain. Reasonable estimates[19] of these parameters are $p = 2$ or 3 and κ decreasing in proportion to $\bar{v}_{2C}$ from a maximum value of 20 at $\bar{v}_{2C} = 1.00$. For a trifunctional network free of defects $(\mu/\xi) = 2$, and F_3 should increase from 0.33 (for the phantom network limit, with $K = 0$) to approximately 0.79 (for the affine limit, with $K = 1 - v_{2m}^{2/3}$).[17,19] Two illustrative theoretical curves, calculated for $p = 2$ and 3,[19] are shown in Figure 5. Although the latter curve gives a somewhat better fit of the experimental results, both give satisfactory agreement, particularly in consideration of the very large uncertainty[8] in the interpretation of such swelling results.

The experimental values of F_4 for the corresponding tetrafunctional networks are located by the points shown in Figure 6, and give the average value of 0.65 ($\pm$0.10). For the corresponding theoretical values, $(\mu/\xi) = 1$, and F_4 should increase from 0.50 to approximately 0.85 as the deformation approaches the affine limit. The two illustrative theoretical curves, included in Figure 6, are again in good agreement with experiment. The results clearly demonstrate that increase in junction functionality significantly increases F_ϕ. The deformation becomes more nearly affine since, as already mentioned, cross-links acting as junctions for four chains are more severely constrained by chain-junction entanglements than are cross-links acting as junctions for three chains.

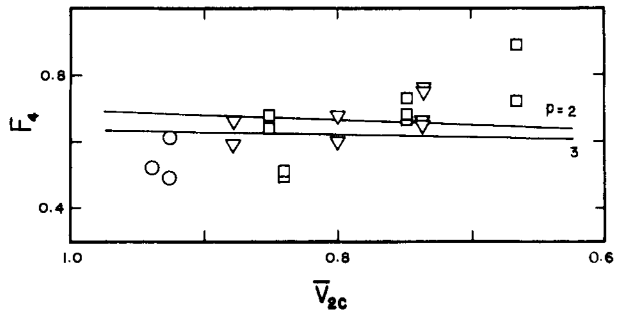


Figure 6. The factor characterizing the extent to which the deformation in swelling approaches the affine limit for the tetrafunctional networks.

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(28) Some related experimental results have been obtained by Valles and Macosko,[4,9] who apparently compare their values of the low deformation modulus with the theoretical predictions[16,17] for the high deformation limit. They also make the assumption, incorrectly in our view, that very large numbers of interchain entanglements trapped during the network formation contribute as effectively to the equilibrium elastomeric properties of a network as they do to the viscoelastic properties of the uncross-linked polymer.
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