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ELASTIC PROPERTIES OF MODEL POLYMER NETWORKS

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Abstract - Polymer networks prepared in such a way as to have known structural characteristics are of fundamental importance in the establishment of reliable structure-property relationships for elastomeric materials. The synthesis and utilization of such "model" elastomers is illustrated using unfilled polydimethylsiloxane (PDMS) networks prepared by two highly selective techniques: (i) the end-linking of hydroxyl-terminated PDMS chains of known molecular weight and molecular weight distribution, by means of either a tetrafunctional or trifunctional silicate, and (ii) the end-linking of vinyl-terminated chains and cross-linking of vinyl-substituted chains using a number of silanes designed to yield a wide range in junction functionality. The series of model PDMS networks thus obtained were investigated with regard to their stress-strain isotherms in elongation up to their rupture points, and their equilibrium swelling in a thermodynamically good solvent. The results provide important information on the dependence of elastic properties on the structural characteristics of the networks, including (i) the average molecular weight of the network chains, (ii) the network chain length distribution, (iii) the limited extensibility of the network chains, (iv) the functionality of the network junctions, and (v) the presence of dangling-chain irregularities.

INTRODUCTION

Establishment of reliable structure-property relationships for elastomeric materials requires, of course, detailed information on network structure. This is seldom available for a typical polymer network because such materials are generally prepared by introducing cross-links between the chains in a random, essentially uncontrolled manner (1,2). As a result, there is no independent knowledge of the crucially important average molecular weight M_c between cross-links and the distribution about this average. Furthermore, it is impossible to vary the cross-link functionality ϕ, since the joining of a pair of segments from two chains will almost invariably give a junction of functionality four. What is obviously required is the preparation of "model" elastomers, i.e., polymer networks having controllable and independently known structural characteristics (3).

Such model networks are prepared by very specific chemical reactions in which the network cross-links are introduced in a carefully controlled manner. For example, polydimethylsiloxane (PDMS) networks of this type have been prepared by end-linking hydroxyl-terminated chains by means of a silicate (3-11), and vinyl-terminated or vinyl-substituted chains with a silane containing active hydrogen atoms (3,12-19). In this approach, chemical analysis and viscometric and gel permeation chromatographic (GPC) measurements are generally carried out on the chains prior to their cross-linking, in order to determine the number-average molecular weight M_n between the potential cross-linking sites. In the case of chains with reactive groups only at the ends, the GPC measurements provide the distribution of M_n as well. Networks then prepared by exclusively and exhaustively reacting these groups with a multi-functional cross-linking agent have known structures in that (i) the molecular weight M_c between cross-links is simply M_n, (ii) the distribution of M_c is also that of M_n, (iii) the functionality ϕ of the cross-links is the same as that of the cross-linking agent, and (iv) the incidence of dangling-end network imperfections is very small.

PDMS model networks of the type described are used to illustrate several aspects of this approach to a better understanding of rubberlike elasticity. The first involves the characterization of non-Gaussian effects related to limited chain extensibility (10,11). Such an investigation requires the use of non-crystallizable polymer networks (20,21) and, unfortunately, elastomers of this type generally can not be extended sufficiently to exhibit such effects. The required increase in maximum extensibility can be achieved, however, by decrease in the number of network imperfections, specifically dangling chain ends. The advantage of using "model" networks made by linking polymer chains exclusively and exhaustively through (hydroxyl) groups placed at their ends is that they have very few, if any, of these irregularities. It was found that networks having a bimodal distribution of very short and

relatively long chains showed the greatest promise in this regard (10,11). Possibly the short chains are important because of their very limited extensibility, with the long chains somehow inhibiting the growth of rupture nuclei and thereby making possible the high elongations required for the non-Gaussian effects to be discernible.

The second illustrative study involves the characterization of the dependence of elastomeric properties on junction functionality (18). The PDMS model networks best suited for this purpose are prepared using an addition reaction between chain vinyl groups and the active hydrogen atoms on a multifunctional silicon hydride (3,12-19). The reaction is particularly versatile in that it can yield a wide range of junction functionalities through the use of cross-linking agents of the type $[OSi(CH_3)H-]_x$, with $x \geq 4$. This type of linear or cyclic molecule can be used with siloxane polymers having vinyl groups either as chain ends (in which case stoichiometric equivalence between hydrogen atoms and vinyl groups would yield networks having $\phi = x$)(12,13,16,18), or as side-group substituents along the chain backbone (which would give $\phi = 2x$) (14,15,17,18). Other, lower, values of ϕ can be obtained, at least as average, approximate values, by using more than the stoichiometrically required amounts of the cross-linking agent.

The final topic is related to the fact that the number of chain-end irregularities in model networks may be controlled through adjustment of the stoichiometric ratio of reactants. Perfect stoichiometric balance should give a very nearly perfect network in this regard, with decrease in the amount of end-linking reactant giving an increase in the number of dangling ends. Such networks are ideal for investigating the effect of these irregularities on elastomeric properties since the method of preparation permits control of both the number and length of the dangling chains.

NON-GAUSSIAN EFFECTS RELATED TO LIMITED CHAIN EXTENSIBILITY

Stress-Strain Isotherms

The quantity of primary interest here is the elastic modulus or reduced stress defined by (4,22-25)

$$[f^*] \equiv f v_2^{1/3}/[A^*(\alpha - \alpha^{-2})] \tag{1}$$

where f is the equilibrium value of the elastic force, v_2 is the volume fraction of polymer in the network during the stress-strain measurements, A^* is the undeformed cross-sectional area, and $\alpha = L/L_i$ is the relative length of the sample. Isotherms were represented by the semiempirical equation of Mooney and Rivlin (2,26)

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \tag{2}$$

in which $2C_1$ and $2C_2$ are constants independent of α. Typical isotherms are shown in Fig. 1. They were obtained using different proportions of long and short chains and thus serve to illustrate the effect of average network chain length. Other series of isotherms (10) show the effect of temperature and the effect of degree of swelling of the network.

The first important observation is that the isotherms show the linearity specified in Eqn.(2) only at low and moderate elongations. At high elongations, there is unquestionably an anomalous upturn in the modulus. The increases in $[f^*]$ are generally quite large, but it is important to note that they seem to be qualitatively different from those generally observed in previous investigations. Specifically, these upturns are gradual, whereas in networks in which strain-induced crystallization or other reinforcement is thought to occur, they are generally more abrupt, frequently corresponding to an almost vertical rise in $[f^*]$ at an elongation only slightly larger than that of at which the increase is first discernible (20,21). Deformations in this range should be highly non-affine with the strain being reapportioned within the network structure so as to avoid any chain being stretched to its maximum length until no further reapportioning is possible. The increase in force arising from limited chain extensibility was therefore predicted (10,20) to be very gradual, as finally observed in the present experiments. Second, the isotherms were highly reversible. Most important, this reversibility occurred even in going from the upturn portion of an isotherm back to the linear portion; such reversibility does not occur when the upturn is due to strain-induced crystallization (27). Third, in the present case the increases in $[f^*]$ were found to persist even to temperatures nearly 200°C above the normal melting point of PDMS, and even at very high degrees of swelling (10). This is not found to be the case in networks undergoing strain-induced crystallization (20). Finally, x-ray fiber diagrams taken on one of the sample strips just prior to rupture showed no evidence whatever of crystallization, in spite of the large upturn in modulus observed for this particular sample (10). These four important observations thus suggest that these results represent the first unambiguous demonstration of the effect of limited chain extensibility on the elastic properties of a polymer network.

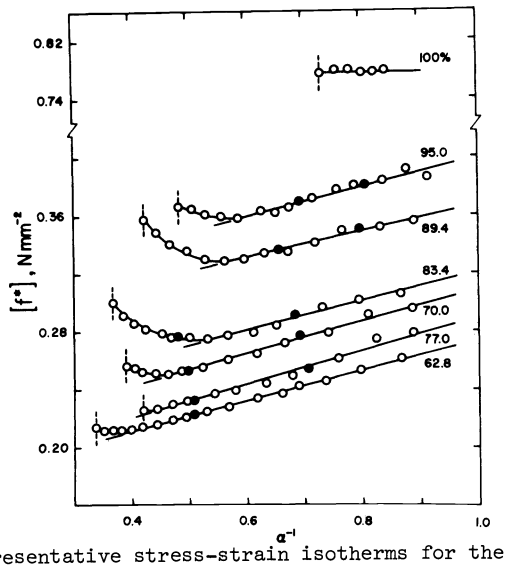

Fig. 1. Representative stress-strain isotherms for the PDMS bimodal tetrafunctional networks in the unswollen state, in elongation at 25°C (10). Each curve is labelled with the mol % of the much shorter chains ($10^{-3}M_n$ = 1.10 vs. 18.5), and the curves thus show the effect of average chain length on the form of the isotherms. The open circles locate the results gotten using a series of increasing values of the elongation α, and the filled circles the results obtained out of sequence to test for reversibility. The vertical dotted lines show the values of α at which rupture occurred, and the short extensions of the linear portions of the isotherms help locate the values of α at which the upturn in the reduced stress [f*] first becomes discernible.

The values α_u of the elongation at the upturn are shown for the tetrafunctional and trifunctional PDMS networks in Fig. 2. There is a significant increase in α_u with increase in

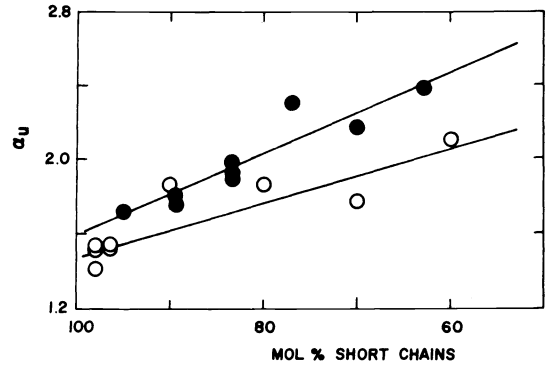

Fig. 2. Values of the minimum elongation at which the upturn in the reduced stress in the PDMS networks is discernible, shown as a function of network composition. The filled circles locate the results obtained for the tetrafunctional networks (10) and the open circles the results (11) for the corresponding trifunctional networks which had been obtained under the same conditions (25°C, in the unswollen state).

average chain length, as would be expected for limited chain extensibility; having fewer short chains permits more extensive reapportioning of the strain within the network, with a corresponding increase in extensibility. The basic process is illustrated schematically in Fig. 3. The present results thus confirm the markedly non-affine character of the deformation in the region of high elongation. Although two least-squares lines are shown for the two sets of data in Fig. 2, a single line would have represented all of the data to within an average of ± 8%. Since this is approximately the uncertainty involved in locating the values of α_u, there does not seem to be a significant dependence of the upturn on junction functionality, at least for the values ϕ = 4 and 3 considered here (10). Although the deformation is non-affine in the vicinity of the upturn, it is possible to provide at least a semi-quantitative interpretation of these results in terms of the network chain dimensions.

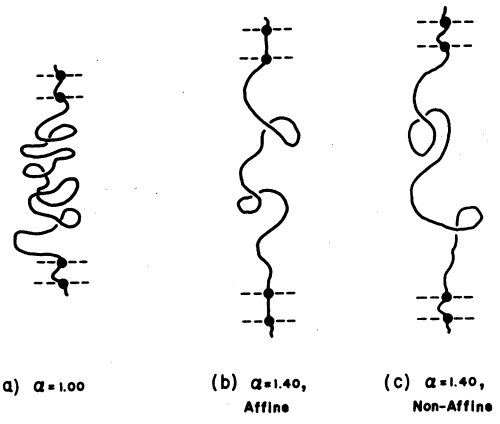

Fig. 3. The effect of deformation on an idealized network segment consisting of a relatively long chain bracketed by two very short chains (10). In the affine assumption, the short chains would be elongated from their undeformed states (a) to essentially their maximum extensibility (b). In the non-affine case (c), however, most of the strain would be transferred to the longer, more easily deformable chains with which the short chains communicate.

At the beginning of the upturn, the average extension r of a network chain having its end-to-end vector along the direction of stretching is simply the product of the unperturbed dimension (10,28) $\langle r^2 \rangle_o^{1/2}$ and α_u. Similarly, the maximum extensibility r_m is the product of the number of skeletal bonds and the factor 1.34Å which gives the axial component of a skeletal bond in the most extended helical form of PDMS (10). The ratio r/r_m at α_u thus represents the fraction of the maximum extensibility occurring at this point in the deformation. The values for both types of networks indicate that the upturn in modulus generally begins at approximately 60-70% of maximum chain extensibility (10,11).

The values of the elongation α_r at which rupture occurred are presented in Fig. 4. As

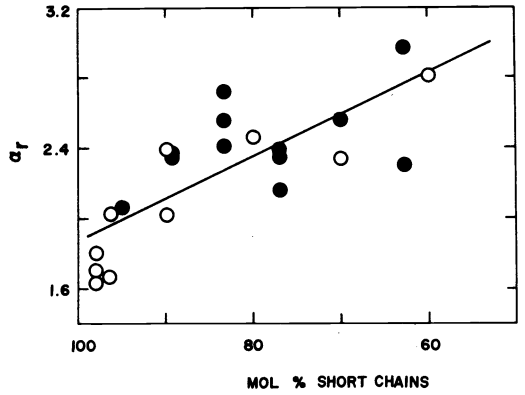

Fig. 4. Values of the maximum extensibility (elongation at rupture) shown as a function of network composition (10,11). See legend to Fig. 2.

expected, α_r increases with increase in average chain length. The least-squares line shown gives a satisfactory representation of all the data, indicating that α_r does not change significantly upon chainge in ϕ from 4 to 3. The corresponding values of r/r_m show that rupture generally occurred at approximately 80-90% of maximum chain extensibility. These quantitative results on chain dimensions are very important but may not apply directly to other networks, in which the chains could have very different configurational characteristics and in which the chain length distribution would presumably be quite different from the very unusual bimodal distribution intentionally produced in the present networks.

The ultimate strength of the networks was taken to be the modulus $[f^*]_r$ at the rupture point, values of which are shown in Fig. 5. The modulus at the rupture point decreases with increase in average chain length (decrease in degree of cross-linking); although a dependence of $[f^*]_r$ on ϕ may be obscured by the scatter in these results, $[f^*]_r$ does not seem to

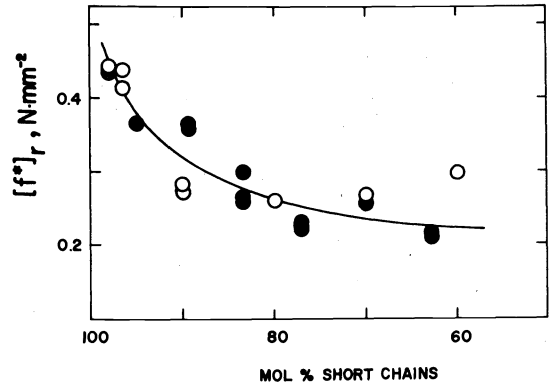

Fig. 5. Values of the ultimate strength (modulus at rupture) shown as a function of network composition (10,11). See legend to Figure 2.

change upon change in ϕ from 4 to 3. This would be rather different from the case of the more nearly monodisperse PDMS networks, which did not show any upturn at all; these networks do exhibit an increase in $[f^*]_r$ with increase in ϕ (18).

It is also of interest to compare the values of r/r_m at the beginning of the upturn with some recent theoretical results (29) on distribution functions for PDMS chains of finite length. Of relevance here are the calculated values of r/r_m at which the Gaussian distribution function starts to overestimate the probability of extended configurations, as judged by comparisons with the results of Monte Carlo simulations. Two sets of results were reported, for n = 20 and 40 skeletal bonds, and yield 0.89 and 0.80 for the corresponding threshold values of r/r_m (29). Only two of the networks studied here have values of n close to this range. The one having $10^{-3}M_n$ = 1.10 (n = 29.6) ruptured, presumably adventitiously, at r/r_m = 0.81, which is below the value 0.85 at which the upturn would be expected on the basis of the theoretical results (29). The second, with $10^{-3}M_n$ = 1.95 (n = 52.6) would be expected to show an upturn at r/r_m a little less than 0.80. The observed value was 0.77, which is thus in excellent agreement with theory.

Some Practical Implications

The end-linked PDMS networks have unusually good ultimate properties. In particular, the bimodal networks consisting of mixtures of relatively long and very short chains are tough elastomers, exhibiting very large values of the amount of work required to bring about rupture. This is obviously of considerable practical as well as theoretical interest.

Swelling Equilibrium

The values of the volume fraction v_{2m} of polymer in each of the tetrafunctional networks at swelling equilibrium in benzene at room temperature are shown as a function of M_n in Fig. 6

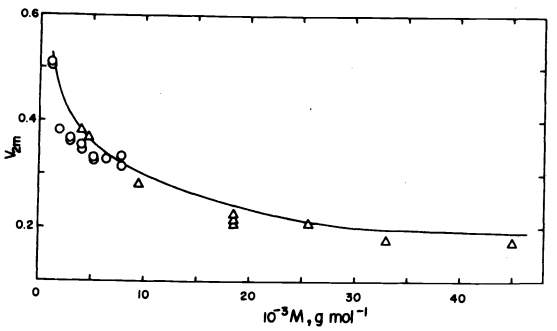

Fig. 6. The volume fraction of polymer at equilibrium (maximum) swelling in benzene at room temperature shown as a function of the molecular weight of the PDMS network chains. The circles (10) and triangles (4,7) correspond to results obtained in three separate studies of the tetrafunctional networks. The line shown was obtained by applying a recent theory of network swelling (30) to the PDMS-benzene system.

(10). The most reliable interpretation of the swelling results utilizes the very recent theory of Flory (30), in which the extent to which the deformation is non-affine 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. The pertinent relationship is given by (7,8,30)

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

in which F_ϕ is a factor characterizing the extent to which the deformation in swelling approaches the affine limit, V_1 is the molar volume of the benzene, v_{2C} is the volume fraction of polymer incorporated in the network structure, and χ_1 is the free energy of interaction parameter (1) between the benzene and the PDMS networks. Reasonable estimates (7,24,30) of these parameters were used to calculate the theoretical line shown in Fig. 6. There is seen to be very good agreement between theory and experiment. Comparisons with the corresponding results for the trifunctional networks (8) indicate that the degree of swelling does not greatly depend on cross-link functionality, in agreement with the conclusions reached in a previous study (18) of more nearly monodisperse PDMS networks covering a much wider range of values of ϕ. The results of this study are summarized in the following Section.

EFFECTS OF JUNCTION FUNCTIONALITY

Stress-Strain Isotherms

These results were analyzed in terms of the elasticity constants $2C_1$ and $2C_2$ appearing in Eqn. (2). Thus, the value of the modulus is $2C_1$ in the limit at large deformation ($\alpha^{-1} \to 0$), and $2C_1 + 2C_2$ in the limit at small deformation ($\alpha^{-1} \to 1$). The theoretical predictions for these related quantities are shown schematically in Fig. 7(11). If the

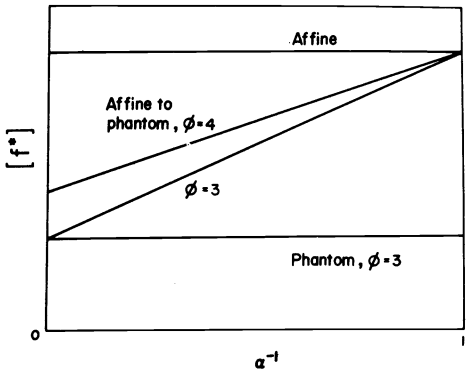

Fig. 7. A schematic diagram (11) qualitatively showing theoretical predictions (31-36) for the reduced stress as a function of reciprocal elongation α^{-1}. In the case of the two limits, the affine deformation and the non-affine deformation in the phantom network limit, the reduced stress should be independent of α. The value for the phantom limit should be reduced, however, by the factor $(1-2/\phi)$ in the case of a ϕ-functional network, as is illustrated for the case $\phi = 3$. The experimentally observed decreases in reduced stress with increasing α are interpreted as resulting from a gradual change from affine to phantom behavior, as portrayed in the two illustrative curves shown for $\phi = 4$ and 3.

displacements experienced by the cross-links in a network are affine (i.e., linear) in the macroscopic deformation, then [f*] should be independent of α ($2C_2 \simeq 0$) (33,34,36). Limiting behavior of this type is shown in the uppermost line in the figure, which should pertain to any value of ϕ (36). This should occur when the cross-links remain firmly embedded in the network structure at all strain levels, as should be the case for PDMS networks at very high cross-link functionality. If, on the other hand, there are significant cross-link fluctuations, the deformation would be non-affine, and this would decrease the elastic effectiveness of the network chains. In the limit of an idealized "phantom" network, in which the chains can freely pass through one another, [f*] would again be independent of α ($2C_2 \simeq 0$) but reduced by the factor $(1 - 2/\phi)$ (31-36). The maximum reduction should occur at $\phi = 3$, where there is a minimum number of chains emanating from a junction point. This is illustrated for the case $\phi = 3$ by the lowermost line in the figure. Such phantom network behavior should occur, at least approximately, in networks in which there is very little overlap in the chain configurational domains. The observation (4,6) that $2C_2 \simeq 0$ for PDMS networks consisting of very short chains is consistent with this expectation.

In general, most real polymer networks have values of [f*] (in the unswollen state) which decrease significantly with increasing α (25), as is illustrated in Fig. 1. This change is interpreted as arising from a gradual transition from affine to phantom behavior as the configurational restraints on the cross-links diminish with elongation (32-36). This is illustrated by the two diagonal lines shown in Fig. 7 for the cases $\phi = 3$ and 4. In this approximate schematic representation, $2C_1 + 2C_2$ and $2C_1$ are given by the intercepts at $\alpha^{-1} = 1$ and 0, respectively, and $2C_2$ therefore by the slope of the line joining the two limits. Increase in ϕ should thus increase $2C_1$, while diminishing $2C_2$ toward zero.

The relevant experimental results are shown in Fig. 8. The values of $2C_1$ qualitatively

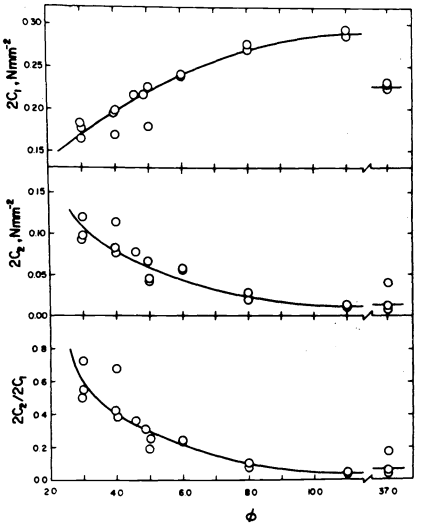

Fig. 8. The dependence of the elasticity constants $2C_1$, $2C_2$, and their ratio $2C_2/2C_1$ on the cross-link functionality of the PDMS networks (18).

follow the expected trend, except for the networks of highest functionality, which may be incompletely end-linked because of possible steric difficulties in having 37 chains terminate within a relatively small volume. Nonetheless, these networks must have junctions of unusually high functionality and are therefore of considerable importance with regard to the effect of ϕ on the other elasticity constant. These results, $2C_2$ and $2C_2/2C_1$ plotted against the functionality, are shown in the two lower portions of Fig. 8. Although some scatter is present, there is obviously good agreement with the theoretical predictions that these quantities approach zero with increasing ϕ.

The elongation results were more quantitatively interpreted in terms of the "structure factors" relating the elasticity constants to the average molecular weight of the network chains. Specifically, the values of $2C_1$ were interpreted using the equation (7,8,10,11,18)

$$2C_1 = A_\phi \rho k T v_{2C}^{2/3} M_n^{-1} \qquad (4)$$

in which A_ϕ is the "structure factor" for the ϕ-functional network, ρ is the density of the network, k is the Boltzmann constant, and T = 298.2K is the absolute temperature. Since $2C_1$ represents the modulus in the limit at large elongation, the deformation should be non-affine, to an extent dependent on ϕ. Specifically, A_ϕ is predicted to be equal to $1 - 2/\phi$ (31,33,34,36). The experimental values of ϕ thus calculated are shown as a function of ϕ in Fig. 9. As can readily be seen, these networks exhibit values of A_ϕ which are somewhat larger than those predicted. This suggests that the deformation may not become non-affine to the extent which would be exhibited by a "phantom network" (33,34). It is important to note, however, that A_ϕ does increase and then level off with increasing ϕ, as predicted by theory.

It is also useful to interpret the modulus in the limit of small deformation since a much shorter extrapolation of the experimental data is required. In this region the deformation should be nearly affine for networks of any functionality and the factor A'_ϕ defined by

$$2C_1 + 2C_2 = A'_\phi \rho k T v_{2C}^{2/3} M_n^{-1} \qquad (5)$$

should always be equal to unity (33,34,36). The observed values of A'_ϕ are also shown as a

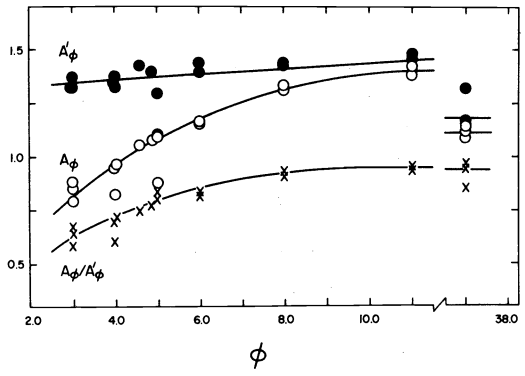

Fig. 9. The dependence of the structure factors A_ϕ, A'_ϕ, and their ratio A_ϕ/A'_ϕ on the cross-link functionality (18).

function of ϕ in Fig. 9. The present results are seen to be in excellent agreement with the prediction that A'_ϕ be relatively independent of ϕ. The ratio A_ϕ/A'_ϕ is predicted to be 1/3 at $\phi = 3$ and to reach an asymptotic value of unity in the limit of large ϕ. The experimental values, included in Fig. 9, are also in good agreement with this prediction.

Structural Information from Chemical Analysis

In the preparation of model polymer networks, it is of course important to carry out the reactions very nearly to completion. For this reason, a series of PDMS networks prepared from the vinyl-terminated and the vinyl-substituted chains were analyzed for unreacted vinyl groups. The technique involves the reaction of a standard solution of iodine monochloride with the polymer network. The ICl which does not react with vinyl groups is converted into iodine, which is then quantitatively reduced to iodide in a titration with standard thiosulfate solution (37).

By these analyses (19), the vinyl end-linking reactions were found to be at least 95% complete, except for one network of very high functionality ($\phi = 37$). The extent of reaction in this case was significantly lower, presumably because of steric interferences with the reaction in the vicinity of the junctions, as was concluded in an earlier investigation (18). The fact that this network had an extent of reaction significantly less than unity (and thus a junction functionality less than 37) is of no consequence since it was used in the previous analysis (18) only to confirm the theoretical prediction (33,34,36) that a network of very high functionality should have a modulus which is essentially independent of elongation. It is of crucial importance, however, that at most only approximately 5% of the vinyl groups are unreacted in the other networks. This is well within the total uncertainties in such experiments.

Lower extents of reaction were obtained for the networks prepared from the vinyl-substituted chains. This is probably due to the fact that these vinyl groups are constrained by two chain sequences instead of one (19). In any case, these results make it possible to obtain a reliable measure of the molecular weight between cross-links, since M_c is simply $M_n/(N_r + 1)$, where N_r is the number of reacted vinyl groups. The values of M_c may then be used in the analysis of the elastic properties of the networks (19).

Swelling Equilibrium

The values of the volume fraction v_{2m} of polymer in each of the networks at swelling equilibrium in benzene at room temperature are shown as a function of ϕ in Fig. 10. As described in the preceding Section, these results were interpreted in terms of the new Flory theory of network swelling (30), the predictions of which are shown by the curve in the figure. The theory is seen to be very successful in that it predicts v_{2m} to be only slightly dependent on junction functionality, and to have a value quite close to that obtained experimentally.

EFFECTS OF DANGLING-END IRREGULARITIES

As already mentioned, the end-linked PDMS networks generally have unusually good ultimate properties. Important comparisons (38) in this regard may be made, for example, with PDMS networks prepared using high-energy radiation (which can give considerable chain scission). This difference in ultimate properties is consistent with the expectation that these model networks have very few imperfections or irregularities such as dangling-chain ends. Accordingly, use of less than the stoichiometrically required amount of end-linking reactant

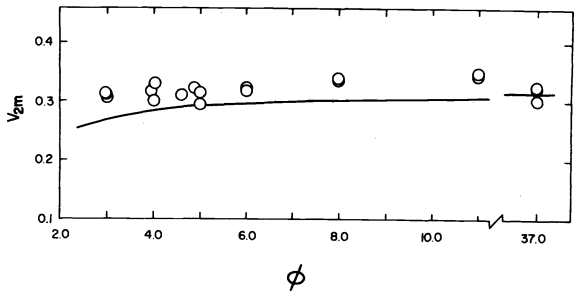

Fig. 10. The volume fraction of polymer at equilibrium swelling in benzene at room temperature shown plotted against the cross-link functionality (18). The circles correspond to the experimental results and the curve represents the prediction of the new Flory theory of network swelling (30).

should increase the number of dangling ends and thus decrease the ultimate properties of the network. Preliminary experimental results (38) are in agreement with this expectation.

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