

Model networks of endlinked polydimethylsiloxane chains. IX. Gaussian, nonGaussian, and ultimate properties of the trifunctional networks

A. L. Andrad, M. A. Llorente, and J. E. Mark

Citation: *The Journal of Chemical Physics* **73**, 1439 (1980); doi: 10.1063/1.440205

View online: <http://dx.doi.org/10.1063/1.440205>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/73/3?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Model networks of endlinked polydimethylsiloxane chains. VII. Networks designed to demonstrate nonGaussian effects related to limited chain extensibility](#)

J. Chem. Phys. **72**, 2282 (1980); 10.1063/1.439472

[Model networks of endlinked polydimethylsiloxane chains. IV. Elastomeric properties of the tetrafunctional networks prepared at different degrees of dilution](#)

J. Chem. Phys. **71**, 682 (1979); 10.1063/1.438354

[Model networks of endlinked polydimethylsiloxane chains. III. Effect of the functionality of the crosslinks](#)

J. Chem. Phys. **70**, 1794 (1979); 10.1063/1.437652

[Model networks of endlinked polydimethylsiloxane chains. II. Viscoelastic losses](#)

J. Chem. Phys. **68**, 2010 (1978); 10.1063/1.435888

[Model networks of endlinked polydimethylsiloxane chains. I. Comparisons between experimental and theoretical values of the elastic modulus and the equilibrium degree of swelling](#)

J. Chem. Phys. **66**, 1006 (1977); 10.1063/1.434056



Model networks of end-linked polydimethylsiloxane chains.

IX. Gaussian, non-Gaussian, and ultimate properties of the trifunctional networks

A. L. Andrad, M. A. Llorente,^{a)} and J. E. Mark

Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio 45221

(Received 14 February 1980; accepted 21 March 1980)

Model elastomeric networks were prepared by end-linking hydroxyl-terminated polydimethylsiloxane chains with a trialkoxy silane. Mixtures of various proportions of relatively long and very short chains were employed, since the resulting "bimodal" networks are of unique importance in characterizing non-Gaussian effects related to limited chain extensibility. Stress-strain isotherms of these trifunctional networks gave values of the elongation at which the modulus begins to increase anomalously, and values of the elongation and modulus at the point of rupture. These results were interpreted in terms of calculated values of the maximum extensibilities of the chains, and were compared with previously reported results on the corresponding tetrafunctional networks in order to characterize the effects of crosslink functionality on these properties. In addition, the elasticity constants characterizing the Gaussian regions of the isotherms, and values of the degree of equilibrium swelling were used to evaluate the most recent molecular theories of rubberlike elasticity, particularly with regard to how the elastic effectiveness of the network chains depends on chain length and extent of deformation.

INTRODUCTION

There are a number of important unresolved issues in the area of rubberlike elasticity which are currently being investigated through the use of "model" polymer networks.^{1,2} These networks are prepared by very specific chemical reactions in which the network crosslinks 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 an alkoxy silane,²⁻⁹ and vinyl-terminated or vinyl-substituted chains with a silane containing active hydrogen atoms.^{2,10-17} In this approach, chemical analysis and viscometric and gel permeation chromatographic (GPC) measurements are generally carried out on the chains prior to their crosslinking, in order to determine the number-average molecular weight M_n between the potential crosslinking sites. In the case of the chains with the reactive groups 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 multifunctional crosslinking agent have known structures in that (i) the crucially important molecular weight M_c between crosslinks is simply M_n , (ii) the distribution of M_c is also that of M_n , (iii) the functionality ϕ of the crosslinks is the same as that of the crosslinking agent, and (iv) the incidence of dangling-end network imperfections is very small. These highly desirable characteristics were exploited in a recent study⁹ of some very unusual tetrafunctional PDMS networks. Essentially "bimodal" networks had been prepared by end linking PDMS mixtures containing various proportions of relatively long and very short chains. The bimodal distribution and the near absence of network imperfections permitted attainment of sufficiently high elongations to

observe and characterize non-Gaussian effects arising from the limited extensibilities of the network chains. The results were unique in that they were not obscured by extraneous complications, such as those resulting from strain-induced crystallization.^{18,19}

The primary purpose of the present investigation was to explore further this general problem of characterizing the effects of limited chain extensibility on equilibrium elastomeric properties, including the ultimate strength and maximum extensibility of a network. More specifically, PDMS model networks having bimodal chain length distributions were again prepared, but with crosslinks of functionality of three instead of the usual functionality of four. The effects of limited chain extensibility on the stress-strain isotherms in elongation were determined and interpreted in terms of the lengths and configurational characteristics of the PDMS chains. Comparisons with the previous results⁹ on the corresponding tetrafunctional networks were then used to elucidate the effect of crosslink functionality on these properties. Although the demonstration and characterization of the non-Gaussian behavior was the primary aim of the investigation, the elastic properties of the networks in the Gaussian region are also of importance with regard to determining the effect of chain length and extent of deformation on the elastic effectiveness of the network chains.

EXPERIMENTAL

The two polymers employed were the same ones used in the previous study⁹ of PDMS bimodal networks, and were among those used in earlier studies³⁻⁵ of the more nearly monodisperse networks as well. They were unfractionated polymers having hydroxyl groups at both ends,⁹ number-average molecular weights M_n of 1.10 and 18.5×10^3 g mol⁻¹, and polydispersity indexes of 2.23 and 1.87.³ They were dried and trifunctionally end linked as described previously.^{5,7} The end-linking

^{a)} Postdoctoral Fellow under the Joint Spain-United States Treaty for Scientific and Technological Cooperation.

TABLE I. Network compositions, non-Gaussian behavior, and ultimate properties.

Composition (short chains)		$10^{-3} M_n$ (calc.)	v_{2C}^a	Upturn		Rupture		
Wt %	Mol %			α^b	r/r_m^c	α^b	r/r_m^c	$[f^*]^d$
74.4	98.0	1.45	0.960	1.49	0.78	1.63	0.85	0.441
				1.53	0.79	1.70	0.88	0.437
				1.41	0.73	1.80	0.93	0.438
62.1	96.5	1.71	0.956	1.54	0.74	1.67	0.80	0.414
				1.53	0.73	2.03	0.97	0.438
34.9	90.0	2.84	0.956	2.00	0.75	2.39	0.89	0.271
				1.86	0.69	2.02	0.75	0.284
19.2	80.0	4.58	0.951	1.86	0.55	2.46	0.73	0.261
12.2	70.0	6.32	0.954	1.75	0.45	2.34	0.60	0.269
8.19	60.0	8.06	0.950	2.10	0.48	3.01	0.69	0.298

^aVolume fraction of polymer incorporated in the network structure.

^bElongation or relative length of the network.

^cLength of a network chain relative to its maximum length.

^dModulus or reduced stress, in N mm⁻².

agent (triethoxyvinylsilane) was present in the amounts required to give exact stoichiometric balance between ethoxy groups and the hydroxyl groups in the PDMS mixtures. The catalyst (stannous-2-ethyl hexanoate) was present in amounts corresponding to 0.6%–1.6% by weight of the polymer. The thoroughly mixed ingredients were poured into aluminum molds and the reaction was allowed to proceed at room temperature for two days. The extensive evidence indicating essentially complete reactions is summarized elsewhere.⁷ The PDMS compositions employed and the average values of M_n calculated for the chains in the various mixtures are given in the first three columns of Table I, and the first two columns of Table II.

The networks thus prepared were extracted and dried as described elsewhere.³ The amount of soluble (uncrosslinked) material removed was found to be approximately 4% of the total weight of polymer. This roughly corresponds to the amount of (2%–6%) of inert dimethylsiloxane cyclics²⁰ generally present in the PDMS samples employed, according to chromatographic measurements.²¹ The precise values of v_{2C} , the volume fraction of polymer incorporated in the network structure, are given in Tables I and II.

The stress-strain isotherms were obtained on (unswollen) strips cut from the various network sheets, using standard techniques,^{3,5,22} at a temperature of 25°C. The strips had cross-sectional areas A^* of approximately 3 mm², and the lengths of the central test portions of the strips were approximately 20 mm. 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. Values of the elastic force f were recorded only after they had become sensibly constant. The elongation was eventually increased to the rupture point of the sample. A number of samples ruptured prematurely because of crazing which occurred during the

extraction procedures. These samples were therefore not used in the analysis of the non-Gaussian behavior and ultimate properties (Table I), but were used to provide information pertaining to the Gaussian regions of the isotherms and to their extents of equilibrium swelling (Table II).

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 the (already extracted) polymer at equilibrium (maximum) swelling.

RESULTS AND DISCUSSION

The stress-strain data were treated in the usual manner.^{3,22-25} Specifically, values of the elastic modulus or reduced stress

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

were plotted against reciprocal elongation, as suggested by the semiempirical equation of Mooney and Rivlin

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

in which $2C_1$ and $2C_2$ are constants independent of α .^{26,27} Typical isotherms are shown in Fig. 1, and demonstrate the fact that the measurements were highly reversible. The upturns in $[f^*]$ occurring at high elongations are very similar to those observed in the corresponding tetrafunctional PDMS networks.⁹ They are clearly due to the limited extensibilities of the network chains, as is demonstrated by (i) the gradual nature of the upturn, (ii) the reversibility observed even in the upturn portion of the isotherms, (iii) the insensitivity of the upturn to temperature and swelling, and (iv) the absence of any x-ray diffraction evidence for strain-induced crystallization.^{9,18,19}

The values α_u of the elongation at the upturn are given in column five of Table I, and are shown as a function

TABLE II. Network compositions, stress-strain characteristics of the networks in the Gaussian region, swelling equilibrium results, and structural information derived therefrom.

Mol % short chains	$10^{-3} M_n$ (calc.)	v_{2C}^a	Elongation					
			$2C_1$ (N mm ⁻²)	A_3	$2C_2$ (N mm ⁻²)	A_3'	$2C_2/2C_1$	v_{2m}^b
100.	1.10	0.958	0.443 0.440	0.21 0.21	0.0188 0.0168	0.22 0.22	0.0425 0.0382	0.400 0.400
98.0	1.45	0.960	0.417 0.416 0.405	0.26 0.26 0.25	0.0223 0.0185 0.0149	0.27 0.27 0.26	0.0534 0.0445 0.0367	0.409 0.402 0.400
96.5	1.71	0.956	0.393 0.378	0.29 0.28	0.0232 0.0297	0.30 0.30	0.0590 0.0784	0.394 0.400
94.9	1.95	0.960	0.226 0.250	0.19 0.21	0.133 0.113	0.30 0.30	0.586 0.452	0.340 0.348
90.0	2.84	0.956	0.209 0.218	0.25 0.26	0.127 0.124	0.41 0.42	0.606 0.571	0.327 0.318
90.0	2.84	0.968	0.206 0.207	0.25 0.25	0.133 0.140	0.41 0.42	0.645 0.678	0.334 0.332
83.0	3.33	0.953	0.193 0.185	0.28 0.26	0.119 0.118	0.45 0.43	0.615 0.639	0.321 0.330
80.0	4.58	0.951	0.192	0.38	0.109	0.59	0.566	0.334
76.9	5.10	0.951	0.171 0.168	0.37 0.37	0.120 0.119	0.64 0.63	0.703 0.704	0.311 0.304
70.0	6.32	0.954	0.190	0.52	0.108	0.81	0.569	0.340
60.0	8.06	0.950	0.212	0.74	0.0784	1.01	0.369	0.326
0.0 ^c	18.5	0.944	0.0902 0.0949	0.72 0.76	0.0760 0.0715	1.33 1.33	0.843 0.753	0.228 0.227

^a Volume fraction of polymer incorporated in the network structure.^b Volume fraction of polymer in the network of swelling equilibrium in benzene at room temperature.^c Reference 7.

of network composition in Fig. 2. There is a significant increase in α_u with increase in average chain lengths, as would be expected for limited chain extensibility; having fewer short chains permits more extensive reappportioning of the strain within the network, with a corresponding increase in extensibility. The present results thus confirm the markedly nonaffine character of the deformation in the region of high elongation.⁹ The corresponding results for tetrafunctional PDMS networks are shown by the filled circles in the figure. Although two least-squares lines are shown for the two sets of data, a single line would have represented all of the data to within an average of $\pm 8\%$. 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 $\phi = 3$ and 4 considered here. Although the deformation is nonaffine in the vicinity of the upturn, it is possible to provide at least a semiquantitative interpretation of these results in terms of the network chain dimensions. 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^{9,28-30} $\langle r^2 \rangle_0^{1/2}$ and α_u . Similarly, the maximum extensibility r_m is the product of the number of skeletal bonds and

the factor 1.34 Å which gives the axial component of a skeletal bond in the most extended helical form of PDMS.⁸ 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 are given in column six of Table I, and indicate that the upturn in modulus generally begins at approximately 60%–70% of maximum chain extensibility. Very similar values were found in the case of the tetrafunctional networks.⁹

The values of the elongation α_r at which rupture occurred are given in column seven of the table and are presented, along with the corresponding results for the tetrafunctional networks, in Fig. 3. As 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 change in ϕ from 4 to 3. The values of r/r_m at the rupture point are given in column eight of the table. They show that rupture generally occurred at approximately 80%–90% of maximum chain extensibility, which is very similar to the result obtained for the tetrafunctional networks.⁹ The ultimate strength of the networks was taken to be the modulus $[f^*]_r$ at the rupture point. The values obtained are given in the last column of Table I and are shown, along

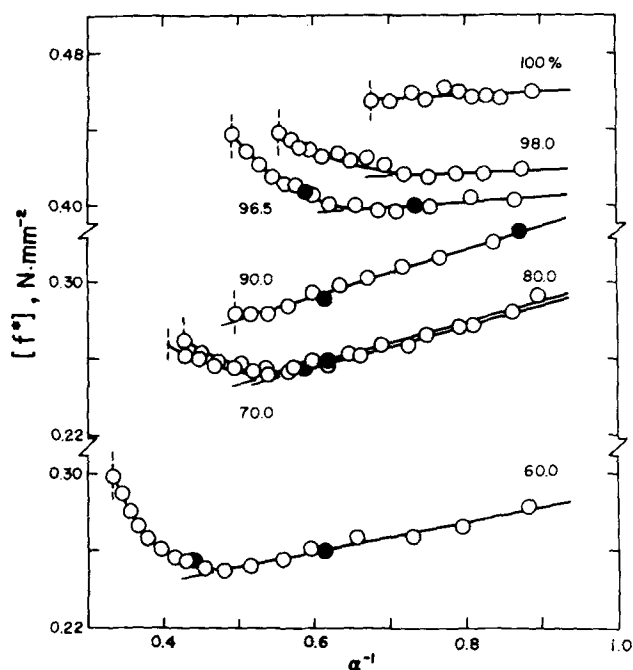


FIG. 1. Typical stress-strain isotherms for the (unswollen) PDMS networks, in elongation at 25 °C. Each curve is labeled with the mol % of the much shorter chains ($10^{-3} M_n = 1.10$ vs 18.5), and the curves thus show the effect of average chain length on the form of the isotherms. The open circles 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 or modulus $[f^*]$ first becomes discernible. The linear portions of the isotherms were located by least-squares analysis.

with the tetrafunctional results, in Fig. 4. The modulus at the rupture point decreases with increase in average chain length (decrease in degree of crosslinking); although a dependence of $[f^*]_r$ on ϕ may be obscured by

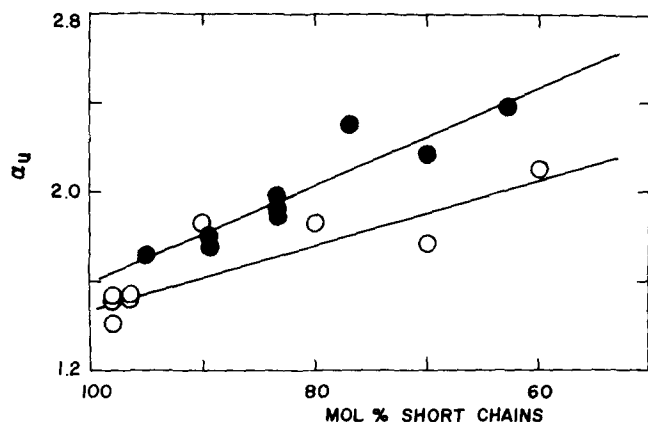


FIG. 2. Values of the minimum elongation at which the upturn in the reduced stress is discernible, shown as a function of network composition. The open circles locate the results obtained for the trifunctional networks, and the filled circles the results⁹ for the corresponding tetrafunctional networks which had been obtained under the same conditions (25 °C, in the unswollen state). Both lines shown were located by least-squares analysis.

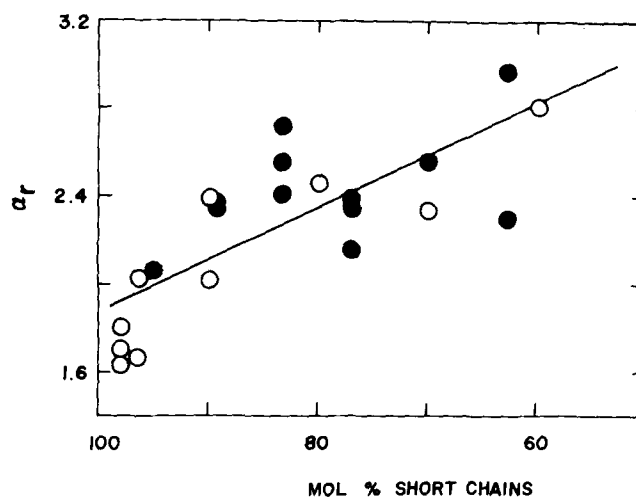


FIG. 3. Values of the maximum extensibility (elongation at rupture) shown as a function of network composition. See the legend to Fig. 2.

the scatter in these results, $[f^*]_r$ does not seem to 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 .¹⁵

The linear, presumably Gaussian, portions of the isotherms were analyzed to provide information on the effect of network structure on the modulus and elastic effectiveness of the network chains. Least-squares analysis was used on these data to obtain values of the elastic constants $2C_1$ and $2C_2$ appearing in Eq. (2); these values are given in columns four and six of Table II. The constant $2C_1$ represents the value of the modulus in the limit at large deformation ($\alpha^{-1} \rightarrow 0$), and $2C_1 + 2C_2$ its value in the limit at small deformation ($\alpha^{-1} \rightarrow 1$). The theoretical predictions³¹⁻³⁶ for these related quantities are shown schematically in Fig. 5. If the displacements experienced by the crosslinks in a

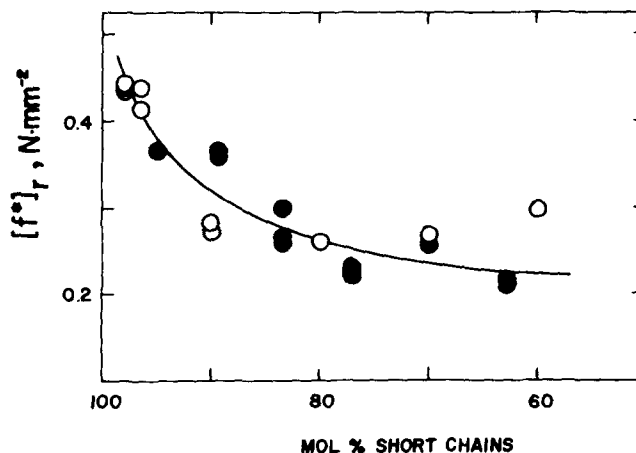


FIG. 4. Values of the ultimate strength (modulus at rupture) shown as a function of network composition. See the legend to Fig. 2.

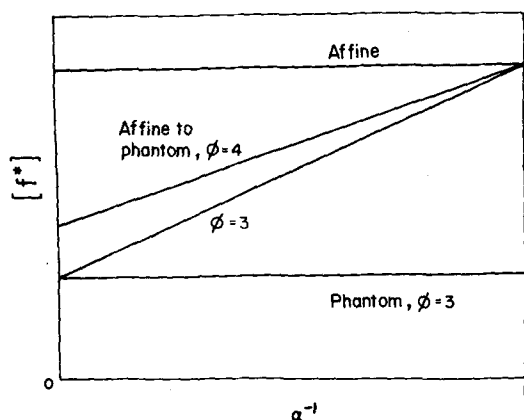


FIG. 5. A schematic diagram qualitatively showing theoretical predictions³¹⁻³⁶ for the reduced stress as a function of reciprocal elongation α^{-1} . In the case of the two limits, the affine deformation and the nonaffine deformation in the phantom network limit, the reduced stress should be independent 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 by the two illustrative curves shown for $\phi = 4$ and 3.

network are affine (i.e., linear) in the macroscopic deformation, then $[f^*]$ should be independent of α ($2C_2 \approx 0$).^{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 crosslinks remain firmly embedded in the network structure at all strain levels, and the observation¹⁶ that $2C \approx 0$ for PDMS networks at very high crosslink functionality is in agreement with this prediction. If, on the other hand, there are significant crosslink fluctuations, the deformation would be nonaffine, 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 ($2C_2 \approx 0$) but reduced by the factor of $(1 - 2/\phi)$.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 of $\phi = 3$ 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^{3,5} that $2C_2 \approx 0$ for PDMS networks consisting of very short chains is consistent with this expectation. Highly swollen polymer networks also exhibit very small values of $2C_2$, and may also fit into this category.^{25,33}

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 crosslinks diminish with elongation.³²⁻³⁶ This is illustrated by the two diagonal lines shown in Fig. 5 for the cases $\phi = 4$ and 3. 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. The observation that $2C_2$ generally decreases with increase in ϕ ,^{5,16} is in agreement with this interpretation of the change in $[f^*]$ with α .

These theoretical concepts were used to interpret the values of $2C_1$ listed in Table II though the equation^{2,5,7}

$$2C_1 = A_3 \rho k T v_{2c}^{2/3} M_n^{-1}, \quad (3)$$

in which ρ is the density of the network, k is the Boltzmann constant, and T is the absolute temperature. The quantity A_3 is the "structure factor" for the trifunctional networks and, since it is proportional to $2C_1$, serves as a measure of the elastic effectiveness of the network chains in the limit at high deformation. The values of A_3 thus obtained are given in column five of the table. The increase in A_3 with increase in M_n is presumably

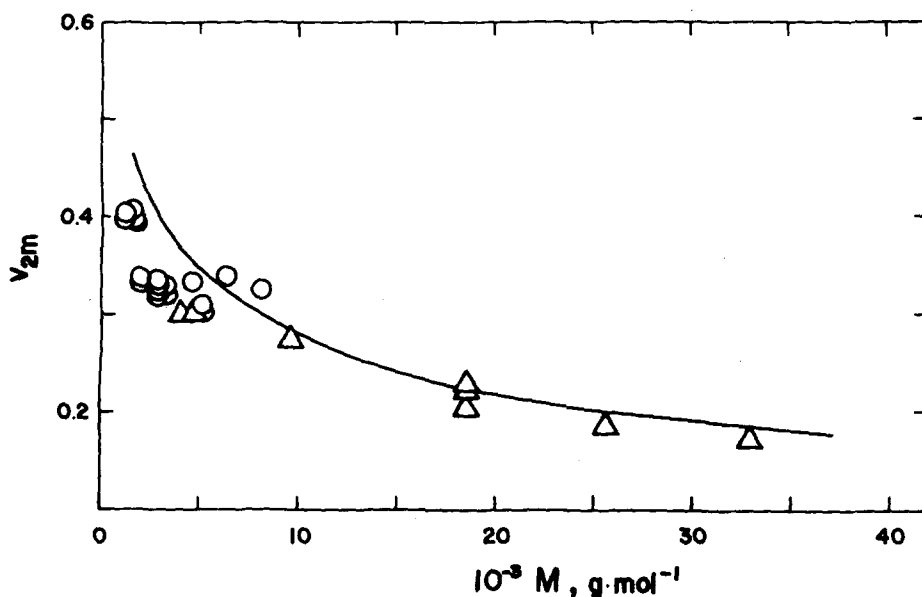


FIG. 6. The volume fraction of polymer at equilibrium (maximum) swelling in benzene at room temperature shown as a function of the molecular weight of the network chains. The open circles correspond to the present experimental values of v_{2m} , which are plotted against the values of M_n shown in Table II; the triangles locate previously published experimental results on other trifunctional PDMS networks which had been end linked in the undiluted state.^{5,7} The line shown was obtained by applying a recent theory of network swelling³⁷ to the PDMS-benzene system.

due to an increase in the severity of the restraints on the crosslinks, thereby preventing the deformation at high α from becoming nonaffine to the extent corresponding to that of a phantom network. In any case, if the results are simply averaged, they yield $A_3 = 0.34$ (± 0.17), which is in excellent agreement with the predicted value $(1 - 2/\phi) = 1/3$. Also, as expected, this result is somewhat smaller than the corresponding result $A_4 = 0.41$ (± 0.14) obtained for the tetrafunctional networks.⁹ The difference is larger and closer to the expected difference in the case of the short-chain networks, where the deformation should be closer to the phantom limit.

It is also possible to provide a similar interpretation of the modulus in the limit at small deformation. The relevant structure factor A'_3 is defined by⁷

$$2C_1 + 2C_2 = A'_3 \rho k T v_{2C}^{2/3} M_n^{-1} \quad (4)$$

and should have values significantly larger than A_3 ; in the limit of a perfectly affine deformation, A'_3 should be equal to unity.³²⁻³⁴ The present results are given in column seven of Table II. The observation that A'_3 is generally not much larger than A_3 could indicate that the deformation of these networks is not close to the affine limit even for very small deformations. At the relatively small values of M_n employed, there may not be sufficient chain interpenetration to embed the junction points in the network structure with the degree of firmness required for an affine deformation. This is consistent with the fact that A'_3 approaches the expected value of unity only for relatively large values of M_n , as was also observed for the tetrafunctional networks.⁹ In any case, the relatively small differences between the values of A'_3 and A_3 is reflected in the unusually small values of the ratio $2C_2/2C_1$. Specific values are given in column eight of the table.

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 the last column of Table II. They are shown as a function of M_n in Fig. 6, which also includes the corresponding results obtained on other trifunctionally end-linked PDMS networks.^{5,7} The most reliable interpretation of the swelling results utilizes the very recent theory of Flory,³⁷ in which the extent to which the deformation is nonaffine depends on the looseness with which the crosslinks 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^{7,37}

$$M_c = -F_3 \rho V_1 v_{2C}^{2/3} v_{2m}^{1/3} / [\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2], \quad (5)$$

in which F_3 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, and χ_1 is the free energy of interaction parameter²⁸ between the benzene and the PDMS networks. Reasonable estimates^{7,24,37} of these parameters were used to calculate the theoretical line shown in Fig. 6. There is seen to be good agreement between theory and experiment.

Comparisons with the corresponding results for the tetrafunctional networks⁹ indicate that the degree of swelling does not greatly depend on crosslink functionality, in agreement with the conclusions reached in a previous study¹⁶ of more nearly monodisperse PDMS networks covering a much wider range of values of ϕ .

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the financial support provided by the National Science Foundation through Grant DMR 79-18903 (Polymers Program, Division of Materials Research), and the postdoctoral fellowship awarded M. A. L. through the Joint Spain-United States Treaty for Scientific and Technological Cooperation.

- ¹P. Rempp and J. E. Herz, *Angew. Makromol. Chem.* **76/77**, 373 (1979).
- ²J. E. Mark, *Makromol. Chem. Suppl.* **2**, 180, 87 (1967).
- ³J. E. Mark and J. L. Sullivan, *J. Chem. Phys.* **66**, 1006 (1977).
- ⁴J. L. Sullivan, J. E. Mark, P. G. Hampton, Jr., and R. E. Cohen, *J. Chem. Phys.* **68**, 2010 (1978).
- ⁵J. E. Mark, R. R. Rahalkar, and J. L. Sullivan, *J. Chem. Phys.* **70**, 1794 (1979).
- ⁶M. A. Llorente and J. E. Mark, *J. Chem. Phys.* **71**, 682 (1979).
- ⁷J. E. Mark and M. A. Llorente, *J. Am. Chem. Soc.* **102**, 632 (1979).
- ⁸M. A. Llorente and J. E. Mark, *J. Polym. Sci. Polym. Phys. Ed.* **18**, 181 (1980).
- ⁹A. L. Andrady, M. A. Llorente, and J. E. Mark, *J. Chem. Phys.* **72**, 2282 (1980).
- ¹⁰E. M. Valles and C. W. Macosko, *Rubber Chem. Technol.* **49**, 1232 (1976).
- ¹¹E. M. Valles and C. W. Macosko, in *Chemistry and Properties of Crosslinked Polymers*, edited by S. S. Labana (Academic, New York, 1977).
- ¹²J. R. Falender, G. S. Y. Yeh, and J. E. Mark, *J. Chem. Phys.* **70**, 5324 (1979).
- ¹³J. R. Falender, G. S. Y. Yeh, and J. E. Mark, *J. Am. Chem. Soc.* **101**, 7353 (1979).
- ¹⁴E. M. Valles and C. W. Macosko, *Macromolecules* **12**, 673 (1979).
- ¹⁵J. R. Falender, G. S. Y. Yeh, and J. E. Mark, *Macromolecules* **12**, 1207 (1979).
- ¹⁶M. A. Llorente and J. E. Mark, *Macromolecules* **13**, 000 (1980).
- ¹⁷M. A. Llorente, A. L. Andrady, and J. E. Mark, *J. Polym. Sci. Polym. Phys. Ed.* (submitted for publication).
- ¹⁸J. E. Mark, *Polym. Eng. Sci.* **19**, 254 (1979).
- ¹⁹J. E. Mark, *Polym. Eng. Sci.* **19**, 409 (1979).
- ²⁰H.-G. Elias, *Macromolecules*, Vol. 2 (Plenum, New York, 1977).
- ²¹J. R. Falender, Dow Corning Corporation (private communication).
- ²²J. E. Mark and P. J. Flory, *J. Appl. Phys.* **37**, 4635 (1966).
- ²³J. E. Mark, *J. Am. Chem. Soc.* **92**, 7252 (1970).
- ²⁴P. J. Flory and Y. Tatara, *J. Polym. Sci. Polym. Phys. Ed.* **13**, 683 (1975).
- ²⁵J. E. Mark, *Rubber Chem. Technol.* **48**, 495 (1975).
- ²⁶M. Mooney, *J. Appl. Phys.* **19**, 434 (1948); R. S. Rivlin, *Philos. Trans. R. Soc. (London) Ser. A* **241**, 379 (1948).
- ²⁷L. R. G. Treloar, *The Physics of Rubber Elasticity* (Clarendon, Oxford, 1975), 3rd edition.
- ²⁸P. J. Flory, *Principles of Polymer Chemistry* (Cornell

- University, Ithaca, 1953).
- ²⁹V. Crescenzi and P. J. Flory, J. Am. Chem. Soc. **86**, 141 (1964).
- ³⁰P. J. Flory, *Statistical Mechanics of Chain Molecules* (Interscience, New York, 1969).
- ³¹W. W. Graessley, Macromolecules **8**, 186, 865 (1975).
- ³²G. Ronca and G. Allegra, J. Chem. Phys. **63**, 4990 (1975).
- ³³P. J. Flory, Proc. R. Soc. (London) Ser. A **351**, 351 (1976).
- ³⁴P. J. Flory, J. Chem. Phys. **66**, 5720 (1977).
- ³⁵B. Erman and P. J. Flory, J. Chem. Phys. **68**, 5363 (1978).
- ³⁶P. J. Flory, Polymer **20**, 1317 (1979).
- ³⁷P. J. Flory, Macromolecules **12**, 119 (1979).