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Model networks of end-linked polydimethylsiloxane chains.

VII. Networks designed to demonstrate non-Gaussian effects related to limited chain extensibility

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End-linking polymer chains by means of a multifunctional cross-linking agent provides an ideal way for obtaining elastomeric networks of any desired distribution of chain lengths. In the present investigation, this technique was employed to give polydimethylsiloxane networks consisting of various proportions of relatively long and very short network chains. The stress-strain isotherms of these networks generally showed an anomalous increase in the modulus at high elongation, and the increase persisted at high temperatures and high degrees of swelling. This non-Gaussian effect was quantitatively correlated with the limited extensibility of the network chains; specifically, the increase in modulus was found to begin at approximately 60%–70% of the maximum extensibility of the network chains, and network rupture at 80%–90%. The elongation at which the increase becomes evident increases with decrease in the proportion of the very short chains, thus verifying the nonaffine nature of the deformation at high elongation. In addition, the elasticity constants characterizing the Gaussian regions of the isotherms, and the values of the degree of equilibrium swelling were used to evaluate the most recent molecular theories of rubberlike elasticity, particularly with regard to the structure factor relating the modulus of an elastomer to the average length or molecular weight of the network chains.

INTRODUCTION

Molecular theories of rubberlike elasticity require the adoption of a distribution function for calculating the probability of any end-to-end separation r of a network chain.^{1,2} The one almost invariably chosen for this purpose, for both the deformed and undeformed states of a network, is the Gaussian distribution function. This function is known to be adequate at low or moderate deformations, but must become increasingly inaccurate for a network chain approaching its maximum extension r_m . The most obvious discrepancy of course is the fact that the Gaussian function assigns zero probability only for infinite r , rather than for any r greater than r_m .

This shortcoming of the Gaussian distribution could be of considerable importance, but the interpretation of the experimental evidence bearing on this point has been very controversial. The modulus of some (unfilled) polymer networks increases markedly in the region of high elongations,^{2–8} and this has frequently been cited as evidence for a non-Gaussian effect arising from the limited extensibility of the network chains.^{2–5,7,8} There is now strong evidence,^{9–15} however, that this interpretation is incorrect, and that the observed increases in modulus were due to internally generated reinforcement of the network structure.^{1,16–18} Such reinforcement would most likely arise from strain-induced crystallization,^{16–19} but also possibly from the formation of hard, glassy domains⁹ in the case of copolymeric elastomers containing sequences of units (such as styrene) which have high glass transition temperatures.²⁰ The major effect of either type of reinforcement would be the generation of “physical” cross links, which would increase the network modulus. Networks to which filler particles

such as carbon black have been added frequently show the increase in modulus, whereas the corresponding unfilled networks either show a less pronounced upturn or none at all.^{9,21–23} Filler particles, however, are known to facilitate strain-induced crystallization,²⁴ to change the effective average chain length and its distribution in an essentially unknown manner, and to make the microscopic strain so inhomogeneous as to preclude reliable interpretation of the results.^{25,26}

The first piece of evidence in support of the above analysis is the clear demonstration that, at least in the case of *cis*-1,4-polybutadiene,^{12,13,15} the increase in modulus disappears upon either increase in temperature or sufficient swelling of the network, both modifications suppressing of course the strain-induced crystallization. The other evidence is less direct, and involves the fact that anomalous behavior has never been observed for any unfilled network which is both incapable of strain-induced crystallization and above suspicion with regard to the complicating presence of hard, glassy domains. Two such polymers which have been studied in this regard are polydimethylsiloxane (PDMS),^{9,11} which has a very low melting point and glass transition temperature (–40° and –127°C, respectively),^{27,28} and atactic poly(ethyl acrylate),⁹ which has a low glass transition temperature (–24°C)²⁸ and is inherently (structurally) incapable of crystallization. Neither of these networks showed the anomalous behavior. There is a frustrating difficulty in the case of this type of network, however; the absence of any self-reinforcing effect generally precludes attainment of the high elongations at which limited chain extensibility could become important. As has been pointed out previously,¹⁰ limited chain extensibility must eventually become important in a network at sufficiently high elongation. The fact that a contribution from this obvious limitation on the network chains has not been demonstrated by any of the experimental

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results obtained to date²⁻¹⁵ indicates that either strain-induced crystallization or network rupture has invariably intervened before the limited extensibility of the network chains could have any discernible effect on the stress-strain isotherms. Limited extensibility effects could occur subsequent to or simultaneous with⁴ strain-induced crystallization, but would be virtually impossible to identify and characterize in its presence.

The only unambiguous way, therefore, for resolving this issue would be through the careful preparation of networks absolutely immune to strain-induced crystallization and the formation of glassy domains, but of very high extensibility in spite of the absence of these self-reinforcing effects. The required increase in maximum extensibility might well be achieved by decrease in the number of network imperfections, specifically dangling chain ends.²⁹⁻³¹ "Ideal" or "model" networks made by linking polymer chains exclusively and exhaustively through functional groups placed at their ends should have very few, if any, of these irregularities. PDMS networks of this type have, in fact, been found to have unusually high extensibilities.^{31,32}

The purpose of the present investigation was therefore to prepare end-linked PDMS networks in a way designed to maximize the likelihood of observing these non-Gaussian effects related to limited chain extensibility, and to characterize any such effects under a variety of experimental conditions. Preliminary experiments indicated that networks having a bimodal distribution of very short and relatively long chains showed the greatest promise in this regard. 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 effect to be discernible. 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 interest with regard to establishing the relationships between the structure of a polymer network and its modulus and equilibrium degree of swelling.

EXPERIMENTAL

The two polymers used were unfractionated samples³³ of PDMS having hydroxyl groups at both ends, number-average molecular weights M_n of 1.10 and 18.5 $\times 10^3$ g mol⁻¹, and polydispersity indexes of 2.23 and 1.87.³² The samples were two of those used in earlier studies,^{32,34} and they were dried and tetrafunctionally end-linked as described previously.^{32,35} The end-linking agent, tetraethyl orthosilicate, 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%–1.9% 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 else-

where.³⁶ 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.

The networks thus prepared were extracted and dried as described elsewhere.³² The amount of soluble (uncross-linked) polymer removed was measured in most cases and was found to be approximately 4% of the total weight of the polymer. This roughly corresponds to the amount (2%–6%) of inert dimethylsiloxane cyclics generally present in the PDMS samples employed, according to chromatographic measurements.³⁷ The precise values of v_{2C} , the volume fraction of polymer successfully incorporated into the network structure are given in column four of the Table.

The stress-strain isotherms were obtained on strips cut from the various network sheets, using standard techniques,^{32,34,38,39} at temperatures ranging from 6 to 150°C. Measurements were carried out on both the unswollen samples and on the samples swollen with linear dimethylsiloxane nonamer.³⁰ The degree of swelling was characterized by the volume fraction v_2 of polymer in the network; values were calculated from the specific volumes of polymer and diluent at room temperature, assuming additivity of volumes. Because of the close similarity between polymer and diluent, these values of v_2 were assumed to apply approximately at the other temperatures as well. (In two cases, v_2 was as low as 0.4, which corresponded to very nearly the maximum degree of swelling attainable.) 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. Finally, x-ray fiber diagrams were taken of one of the strips, at room temperature, at elongations just short of that required for rupture.

Equilibrium swelling measurements were carried out on each of the network strips, in benzene at room temperature, as described previously.³² The extent of swelling was characterized by v_{2m} , the volume fraction of the (already extracted) polymer at equilibrium (maximum) swelling.

RESULTS AND DISCUSSION

Values of the elastic modulus or reduced stress^{32,38-41}

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

were plotted against reciprocal elongation, as suggested by the semiempirical equation of Mooney and Rivlin^{2,42}

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

in which $2C_1$ and $2C_2$ are constants independent of α . The experimental conditions under which the isotherms were obtained are given in columns five and six of Table I,

TABLE I. Network compositions, conditions for stress-strain measurements, non-Gaussian behavior, and elongation at rupture.

Composition (short chains)		$10^{-3} M_n$ (calc)	v_{2C}^a	T (°C)	v_2^b	Upturn		Rupture	
Wt%	Mol%					λ^c	r/r_m^d	λ^e	r/r_m^d
100	100	1.10	0.960	25	1.00	1.37	0.814
					1.00	1.37	0.814
53.4	95.0	1.95	...	25	1.00	1.72	0.772	2.06	0.925
33.4	89.4	2.94	0.969	6	1.00	1.83	0.667	2.30	0.839
					1.00	1.75	0.643	2.35	0.863
				25	1.00	1.80	0.661	2.37	0.870
					0.617	1.89	0.694	2.13	0.782
					0.396	2.17	0.797	2.44	0.896
					1.00	1.72	0.638	2.10	0.778
				50	0.640	1.89	0.700	2.21	0.819
					1.00	1.63	0.614	2.27	0.855
					1.00	2.02	0.761	2.43	0.914
					0.394	1.87	0.704	2.07	0.779
23.0	83.4	3.99	0.969	25	1.00	1.98	0.628	2.56	0.812
					1.00	1.92	0.609	2.41	0.764
					1.00	1.89	0.599	2.72	0.863
				125	1.00	1.89	0.620	2.42	0.794
					0.720	1.82	0.597
				150	1.00	1.85	0.612	2.00	0.661
					1.00	1.89	0.625	2.44	0.807
					1.00	1.89	0.625	2.44	0.807
16.6	77.0	5.10	0.968	25	1.00	2.30	0.649	2.39	0.675
					1.00	2.16	0.610
					1.00	2.34	0.661
12.2	70.0	6.32	0.962	25	1.00	2.17	0.553	2.56	0.653
9.12	62.8	7.57	...	25	1.00	2.30	0.540
					1.00	2.38	0.558	2.97	0.697
0.00 ^e	0.00	18.5	0.926	25	1.00	1.62	0.246
					1.00	1.78	0.270
					1.00	1.87	0.284

^aVolume fraction of polymer successfully incorporated in the network structure.^bVolume fraction of polymer in the network during the stress-strain measurements.^cTotal elongation of the network.^dLength of a network chain relative to its maximum length.^eReferences 32 and 35.

and representative results are shown in Figs. 1–3. The isotherms in Fig. 1 were obtained using different proportions of long and short chains and thus serve to illustrate the effect of average network chain length. Similarly, Fig. 2 shows the effect of temperature, and Fig. 3 the effect of degree of swelling of the network.

The first observation, from all three figures, is that the isotherms show the linearity specified in Eq. (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. Deformations in this range should be highly nonaffine 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^{15,25} to be very gradual, as finally observed in the present experiments. Secondly, as is illustrated by the filled points in the three figures, 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.¹² Thirdly, in the present case the increases in $[f^*]$ persist even to temperatures nearly 200°C above the normal melting point of PDMS (as is illustrated in Fig. 2), and even at very high degrees of swelling (as is illustrated in Fig. 3). This is not found to be the case in networks undergoing strain-induced crystallization.¹⁵ Finally, the 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 sample (89.4 mol % short chains) at 25°C. These four important observations thus suggest that the results shown in Figs. 1–3 are the first unambiguous demonstration of the effect of limited chain extensibility on the elastic properties of a polymer network.

Analysis of the values of the elongation at the start of the upturn and at rupture is best carried out in terms of the total elongations $\lambda_u = \alpha_u v_2^{-1/3}$ and $\lambda_r = \alpha_r v_2^{-1/3}$, defined so as to include the required, additional contribution in the case of the swollen networks. The values of λ_u thus calculated are given in column seven of Table I. As ex-

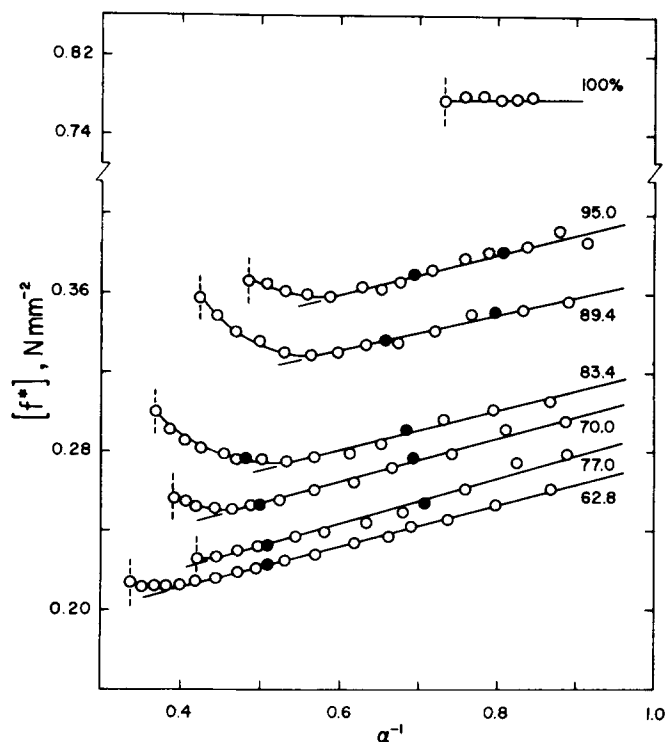


FIG. 1. Representative stress-strain isotherms for the PDMS networks in the unswollen state, in elongation at 25°C. Each curve is labelled with the mol % of the much shorter chains ($10^{-3} M_n = 1.10$ vs 18.5), and the curves thus show the effect of average chain length on the form of the isotherms. 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 linear portions of the isotherms were located by least-squares analysis.

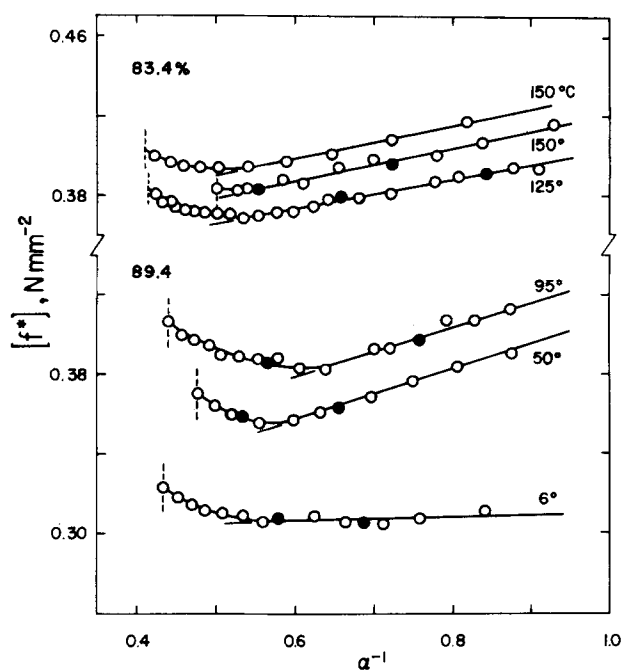


FIG. 2. Typical results obtained to determine the effect of temperature on the stress-strain isotherms. The curves are labelled with the mol % of short chains in the networks and the temperatures at which the elasticity measurements were carried out. See legend to Fig. 1.

pected, they do not show the strong dependence on temperature and degree of swelling that is exhibited in the case of crystallizable networks.^{10,14,15} There is a marked increase in λ_u with increase in average chain length, however, as would be expected for limited chain

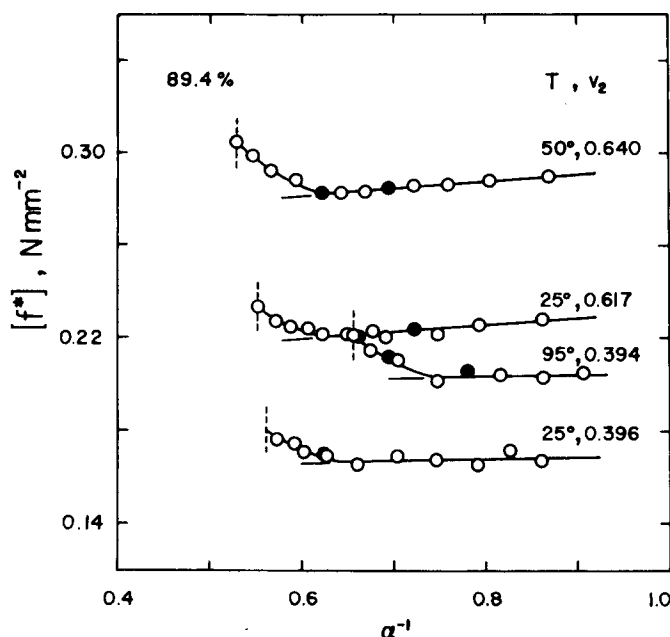


FIG. 3. Typical results obtained to determine the effect of the degree of network swelling on the stress-strain isotherms. The curves pertain to samples taken from the network containing 89.4 mol % of the short chains, and each is identified by the temperature and volume fraction of polymer in the swollen network. See legend to Fig. 1.

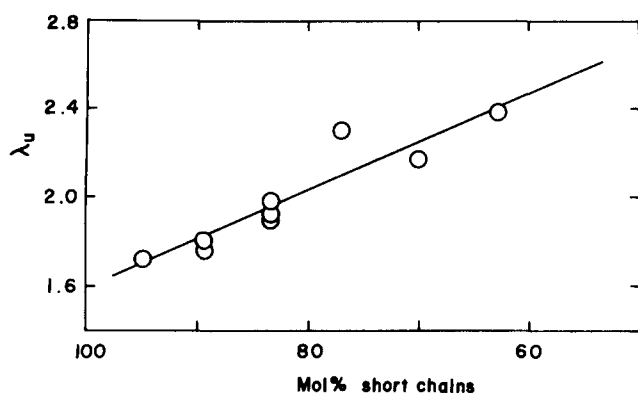


FIG. 4. Values of the minimum elongation at which the upturn in the reduced stress is discernible, shown as a function of network composition. The results pertain to the unswollen networks at 25 °C, and the line shown was located by least-squares analysis.

extensibility, and this is illustrated by the results shown in Fig. 4. In brief, fewer short chains permits more extensive reapportioning of the strain within the network, with a corresponding increase in extensibility. The basic process, already mentioned above with regard to the gradual nature of the upturn is illustrated schematically in Fig. 5. The present results thus confirm the markedly nonaffine character of the deformation in the region of high elongation.

Interpretation of these results in terms of network chain dimensions is somewhat complicated by the fact that the conformation of maximum extension for PDMS is not the all-*trans* ("planar zig-zag") form, as it is for many polymers including polyethylene (PE). This oc-

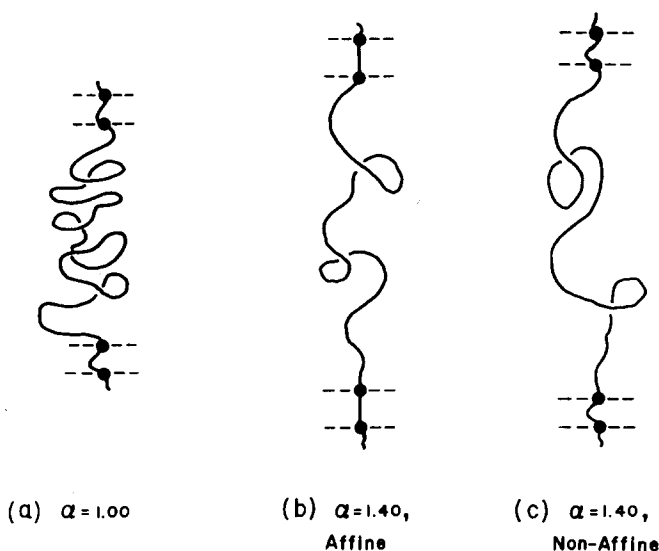


FIG. 5. The effect of deformation on an idealized network segment consisting of a relatively long chain bracketed by two very short chains. In the affine assumption, the short chains would be elongated from their undeformed states (a) to essentially their maximum extensibility (b). In the nonaffine case (c), however, most of the strain would be transferred to the longer, more easily deformable chains with which the short chains communicate.

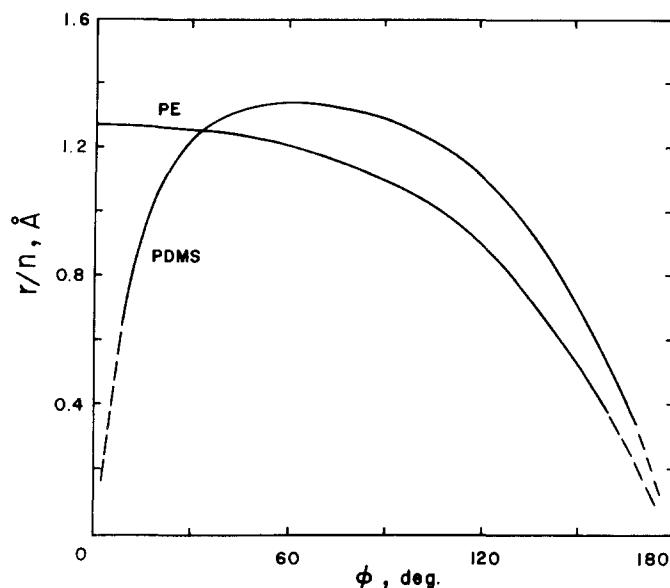


FIG. 6. The end-to-end distance per skeletal bond for regular conformations of polydimethylsiloxane and polyethylene network chains. The maximum in the PDMS curve indicates that the maximum extensibility r_m of this chain molecule occurs at $r_m/n = 1.34$ Å.

curs because the unequal skeletal bond angles in the $[\text{Si}(\text{CH}_3)_2\text{O}]$ chain causes the all-*trans* conformation to form a closed polygon after $360^\circ/(70^\circ-37^\circ) = 10.9$ repeat units.^{43,44} Calculations of its end-to-end distances r were therefore carried out, using skeletal bond angle supplements of 70° and 37° , and skeletal bond lengths l of 1.64 Å.⁴⁴ The conformations of importance are the regular ones (generally helical) and, as a reasonable approximation, the same rotational angle ϕ was assumed to apply to all of the bonds in the chain. The results are shown in Fig. 6. Included for purposes of comparison are the corresponding results for PE $[\text{CH}_2\text{--CH}_2\text{--}]$, which has bond angle supplements of 68° and bond lengths of 1.53 Å.⁴⁴ (The calculations were carried out for $n = 30$ skeletal bonds, but the results are valid for any n greater than approximately 10.) The results for PE verify the obvious fact that the conformation of highest extension is the all-*trans* form ($\phi = 0^\circ$); the all-*cis* form represents a closed polygon having $360^\circ/(68^\circ + 68^\circ) = 2.6$ repeat units. (Steric interferences would prevent the actual chain from forming such compact configurations near $\phi = 180^\circ$, and this part of the curve has therefore been represented by a dotted line.) The results for PDMS show the expected decrease in r near both the all-*trans* form and the all-*cis* form, the latter corresponding to a closed polygon of $360^\circ/(70^\circ + 37^\circ) = 3.4$ units. They also indicate that maximum extension corresponds to $r/n = 1.34$ Å (which occurs at $\phi = 60^\circ$). The maximum extensibility of the chains in each of the PDMS networks described in the table may therefore be calculated from

$$r_m = 1.34 n, \quad (3)$$

which gives values of r_m only 18% below the value nl of a perfectly linear array of the same number of bonds. For the pertinent range $10^{-3} M_n = 1.10$ to 7.57 , n is 29.6 to 204 skeletal bonds.

TABLE II. 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)	T (°C)	ν_2^a	$2C_1$ (N mm $^{-2}$)	A_4	$2C_2$ (N mm $^{-2}$)	A_4'	$2C_2/2C_1$	ν_{2m}^b
100	1.10	25	1.00	0.767	0.361	0.0111	0.366	0.0145	0.506
			1.00	0.770	0.362	0.0265	0.364	0.0344	0.503
95.0	1.95	25	1.00	0.299	0.250	0.101	0.326	0.338	0.371
89.4	2.94	6	1.00	0.299	0.392	0.0111	0.405	0.0373	0.366
									0.361
		25	1.00	0.302	0.377	0.0576	0.439	0.191	...
			1.00	0.277	0.346	0.0904	0.449	0.327	...
			0.617	0.201	0.252	0.0304	...	0.151	...
			0.396	0.161	0.201	0.0083	...	0.0513	...
		50	1.00	0.280	0.330	0.128	0.460	0.457	...
			0.640	0.262	0.309	0.0321	...	0.122	...
		95	1.00	0.306	0.330	0.123	0.424	0.400	...
			1.00	0.376	0.405	0.0397	0.412	0.106	...
			0.394	0.198	0.213	0.0008	...	0.039	...
		25	1.00	0.204	0.346	0.0920	0.501	0.450	0.346
			1.00	0.222	0.377	0.0786	0.499	0.354	0.355
			1.00	0.220	0.372	0.101	0.532	0.459	0.346
			1.00	0.329	0.456	0.0743	0.501	0.226	...
			0.720	0.343	0.475	0.0650	...	0.189	...
		150	1.00	0.337	0.449	0.0842	0.493	0.249	...
			1.00	0.347	0.462	0.0849	0.506	0.244	...
77.0	5.10	25	1.00	0.173	0.373	0.116	0.614	0.672	0.327
			1.00	0.182	0.395	0.0987	0.596	0.542	0.332
			1.00	0.177	0.384	0.108	0.605	0.610	...
70.0	6.32	25	1.00	0.198	0.529	0.112	0.809	0.565	0.327
62.8	7.57	25	1.00	0.167	0.540	0.112	0.878	0.671	0.314
			1.00	0.168	0.543	0.106	0.862	0.629	0.332
0.00 ^c	18.5	25	1.00	0.0958	0.776	0.0427	1.12	0.446	0.207
			1.00	0.0891	0.722	0.0429	1.07	0.481	0.225
			1.00	0.0892	0.715	0.0395	1.03	0.443	0.213

^aVolume fraction of polymer in the network during the stress-strain measurements.^bVolume fraction of polymer in the network at swelling equilibrium in benzene at room temperature.^cReferences 32 and 35.

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

$$r = \langle r^2 \rangle_0^{1/2} \lambda_u, \quad (4)$$

where $\langle r^2 \rangle_0$ is the mean-square end-to-end distance of the chain, as it exists in the unswollen, undeformed network,⁴⁶ i. e., unstretched, and unperturbed by excluded volume effects.¹ The characteristic ratio $\langle r^2 \rangle_0/nl^2$ of high molecular weight PDMS in the undiluted state (of low cohesive energy density) is 7.7 in the vicinity of room temperature,⁴⁶ with a temperature coefficient $d\ln\langle r^2 \rangle_0/dT$ of $0.71 \times 10^{-3} \text{ K}^{-1}$.⁴⁷ Calculations⁴⁴ indicate that for the relatively short chains used in the present investigation the values of $\langle r^2 \rangle_0/nl^2$ near room temperature should increase from approximately 7.0 to 7.5 for

the cited increase in M_n , reaching 7.7 only for the relatively long chains ($10^{-3} M_n = 18.5$) in the network studied previously^{32,35} but included in Table I for purposes of comparison. Values of the important ratio r/r_m at the start of the upturn were thus calculated, with appropriate corrections for the temperature dependence of $\langle r^2 \rangle_0^{1/2}$; the results are given in column eight of the table. It is seen that the upturn begins at approximately 60%–70% of the average maximum extensibility of the network chains. The same calculations were carried out for the values of the elongation λ_r at rupture which were taken from Figs. 1–3 and which are presented in column nine of the table. The corresponding values of r/r_m are given in the last column and indicate that rupture occurred at approximately 80%–90% of the average maximum extensibility. These quantitative results may

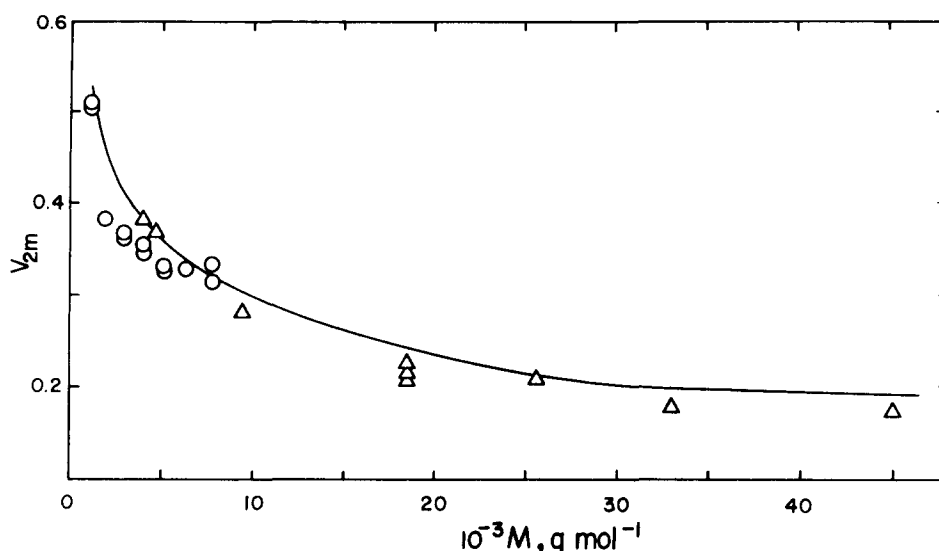


FIG. 7. The volume fraction of polymer at equilibrium (maximum) swelling in benzene at room temperature shown as a function of the molecular weight of the network chains. The open circles correspond to the present experimental values of v_{2m} , which are plotted against the values of M_n shown in Table I; the triangles locate previously published experimental results on other tetrafunctionally end-linked PDMS networks.^{32,35,52} The line shown was obtained by applying a recent theory of network swelling⁵⁴ to the PDMS-benzene system.

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.

It is also of interest to compare the values of r/r_m at the beginning of the upturn with some recent theoretical results⁴⁸ 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 comparison 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 .⁴⁸ 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.⁴⁸ 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.

The linear, presumably Gaussian, portions of the isotherms were analyzed to provide information on the effect of network structure on the modulus. 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 five and seven of Table II. The constant $2C_1$ represents the value of the modulus in the limit of large deformation ($\alpha^{-1} \rightarrow 0$), and $2C_1 + 2C_2$ its value in the limit of small deformation ($\alpha^{-1} \rightarrow 1$). The values of $2C_1$ listed in the table were interpreted using the equation^{32,35,49-51}

$$2C_1 = A_4 \rho k T v_{2C}^{2/3} M_n^{-1} \quad (5)$$

in which A_4 is the "structure factor" for the tetrafunctional network, ρ is the density of the network, k is the Boltzmann constant, and T is the absolute temperature. Since $2C_1$ represents the modulus in the limit of large elongation, the deformation should be nonaffine.⁴⁹⁻⁵¹

The value of A_4 for the nonaffine deformation of a ϕ -functional phantom network is given by $1 - 2/\phi$, and should therefore be $\frac{1}{2}$ for the present tetrafunctional case. The values of A_4 thus calculated are given in column six of Table II. If simply averaged, they yield 0.42 (with a standard deviation of 0.14), which is smaller than the result 0.71 previously obtained for other tetrafunctionally end-linked PDMS networks having values of M_n comparable to those in the present investigation.^{32,35} The difference may be due to the very unusual chain length distribution used in the present study. In any case, the present result is obviously in good agreement with the expected value of $1/2$.⁴⁹⁻⁵²

In the case of the unswollen networks, it is also possible to provide a similar interpretation of the modulus in the limit of small deformation. The relevant structure factor A'_4 is defined by³⁵

$$2C_1 + 2C_2 = A'_4 \rho k T v_{2C}^{2/3} M_n^{-1} \quad (6)$$

and should have values significantly larger than A_4 . In the limit of a perfectly affine deformation, A'_4 should be equal to unity.⁴⁹⁻⁵¹ The present results are given in column eight of Table II and yield 0.59 (with a standard deviation of 0.23). The observation that A'_4 is not much larger than A_4 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. In any case, the relatively small difference between the values of A'_4 and A_4 is reflected in the unusual small values of the ratio $2C_2/2C_1$. Specific values are given in column nine 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 column ten of Table II. They are shown as a function of M_n in Fig. 7, which also includes the corresponding results obtained on other tetrafunctionally end-linked PDMS networks.^{32,35,53} The most reliable interpretation of the swelling results utilizes the very recent theory of Flory,⁵⁴ 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. The pertinent relationship is given by⁵⁴

$$M_c = -\left(\frac{1}{2}\right)\rho V_1 v_{2c}^{2/3} v_{2m}^{1/3} (1+K) / [\ln(1-v_{2m}) + v_{2m} + \chi_1 v_{2m}^2] \quad (7)$$

in which M_c is the molecular weight of the network chains, $V_1 = 89.08 \text{ cm}^3 \text{ mol}^{-1}$ is the molar volume of the benzene, and χ_1 is the free energy of interaction parameter¹ between the benzene and the PDMS networks. The required values of χ_1 were obtained from published results,⁴⁰ which indicate $\chi_1 = 0.484 + 0.330 v_{2m}$ for the pertinent range of v_{2m} . The quantity 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 of these parameters are $p=2$, and $\kappa=20$.^{35,54} Values of $1+K$ were obtained by interpolation of published values⁵⁴ of this factor for illustrative values of v_{2m} . The resulting theoretical curve for v_{2m} as a function of M_c (or M_n) is shown in Fig. 7, and is seen to be in good agreement with the experimental results.

CONCLUDING COMMENTS

The most important results of this investigation involve the quantitative characterization of the effects of limited chain extensibility on the stress-strain properties of an amorphous polymer network. These are apparently the only reliable results of this type available at the present time and should be extremely useful for the evaluation of non-Gaussian theories of rubberlike elasticity. Such work is in progress.

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⁵²If the extractable portions of the networks are considered to

be polymer chains that could have reacted, rather than inert material (an incorrect assumption, in our view), then the values of the structure factors would be increased to approximately 0.8, which is still in reasonable agreement with theory. Since the theory involved^{49-51,54} intentionally ignores entanglements, the results of either interpretation thus support the assumption that such entanglements do not significantly contribute to *equilibrium* elastomeric properties. Prior to the chain end-linking and cross-linking process, some of the chains were relatively short, but it is difficult to relate this objectively to the average degree of interchain entangling in the resulting network.

⁵³The swelling results obtained in the first study³² of the tetrafunctional PDMS networks were interpreted but not used in a later investigation.³⁵ Some of the molecular weights listed there³⁵ were incorrect, the correct values for $v_{2m} = 0.153$, 0.178, 0.208, 0.281, 0.368, and 0.381 being $10^{-3} M_c = 56.6$, 40.3, 27.4, 11.3, 4.53, and 4.07.

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