Model Networks of End-Linked Polydimethylsiloxane Chains. XII. Dependence of Ultimate Properties on Dangling-Chain Irregularities

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Synopsis

Elastomeric networks were prepared by end-linking vinyl-terminated polydimethylsiloxane (PDMS) chains having number-average molecular weights of 11.3×10^3 g mol^{-1}. The tetra-functional end-linking agent, $Si[OSi(CH_3)_2H]_4$, was used in varying amounts smaller than that corresponding to a stoichiometric balance between its active hydrogen atoms and the chain vinyl groups. The number of dangling-chain irregularities thus introduced into the networks was directly determined by iodometric titration for unreacted vinyl groups. The (unfilled) PDMS networks thus obtained were studied in elongation to their rupture points at 25°C (a temperature sufficiently high to prevent complications from strain-induced crystallization), and in swelling equilibrium in benzene at room temperature. Small to moderately large proportions of dangling chains were found to have less of an effect on the elongation modulus than might be expected, and similarly a relatively small effect on the degree of equilibrium swelling. Most importantly, comparisons of constant values of the high deformation modulus show that dangling-chain irregularities decrease both the maximum extensibility of a network and its ultimate strength.

INTRODUCTION

Rupture of an elastomeric network may be faciliated by weak points such as might occur, for example, at imperfections or irregularities in the network structure.[1-4] One of the most important molecular irregularities of this type is the dangling chain, i.e., a chain attached to the network at only one of its ends. It is therefore of interest to note that the number of such dangling chains can depend greatly on the (number-average) molecular weight M_n of the uncross-linked polymer and the method used to cross-link it into an elastomeric material. For example, linking chains exclusively through functional groups placed at their ends should yield a network having few, if any, dangling chains.[5-12] A network prepared by randomly joining segments from different chains by means of a chemical agent such as a peroxide, however, would generally have more dangling chains, the minimum number being inversely proportional to M_n of the starting polymer.[1] At the other extreme would be networks cross-linked by means of high-energy radiation. Such elastomers can have very large numbers of dangling

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chains arising from chain scissions occurring during the cross-linking process.[13-15]

In spite of the obvious importance of dangling-chain irregularities, relatively little has been done to characterize their effects on elastomeric properties. Part of the problem is, of course, obtaining information on the number of such irregularities in the networks being investigated. In spite of this difficulty, some useful information has been obtained on the effect of dangling chains on (i) equilibrium compression moduli and degrees of swelling,[16,17] (ii) elongation and ultimate strengths in continuous extension,[1,16] (iii) visco-elastic properties in free[18] and forced[19] oscillations, and (iv) fatigue lifetimes under alternating stress amplitudes.[20] The effects of these irregularities on the ultimate properties under near-equilibrium conditions are essentially entirely unexplored, however, and the purpose of the present investigation is to provide some information of this type using elastomeric networks of polydimethylsiloxane (PDMS).

Some very useful information on PDMS networks relevant to this issue was already available, or could be easily obtained by carrying out measurements on materials that had been prepared for other purposes.[5-12,21-31] Typical results of this type for the tetrafunctional networks are shown in Figures 1 and 2. The ultimate properties considered are the maximum extensibility α_r (the relative length at rupture) and ultimate strength $(f/A^*)_r$ (where f is the elastic force at rupture and A^* is the undeformed cross-sectional area of the sample). They are shown as a function of the molecular weight M_c between cross-links in the
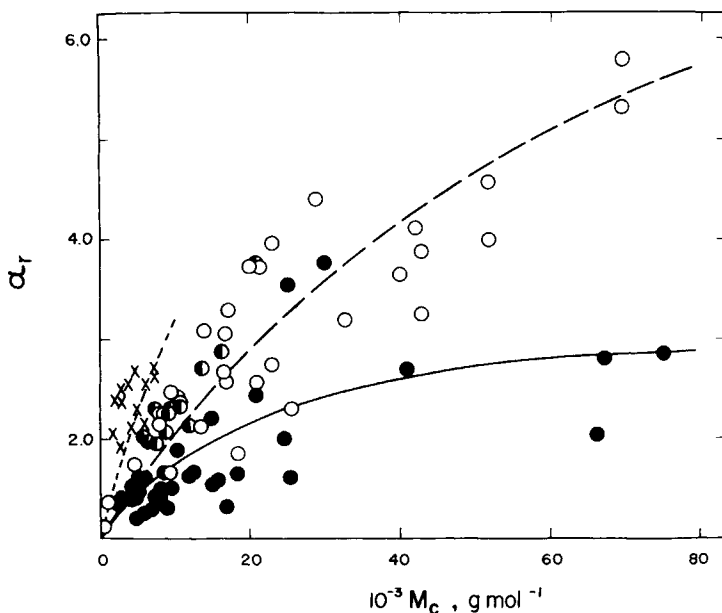

Fig. 1. Values of the maximum extensibility (elongation at rupture) shown as a function of the approximate molecular weight M_c between cross-links for (unfilled) polydimethylsiloxane networks at 25°C. The results pertain to networks prepared and studied in a series of previous investigations and are typical for the types of cross-linking techniques employed: (i) selectively end-linking a mixture of relatively long and very short chains to give a "bimodal" network (- -X- -) (Refs. 8 and 12), (ii) selectively linking a (unimodal) sample of chains either through their ends or side-chains (- -O- -) (Refs. 5, 12, 22, 23, and 30), (iii) peroxide curing (◑) (Refs. 22, 23, and 31), and (iv) radiation curing (–●–) (Refs. 21 and 26).
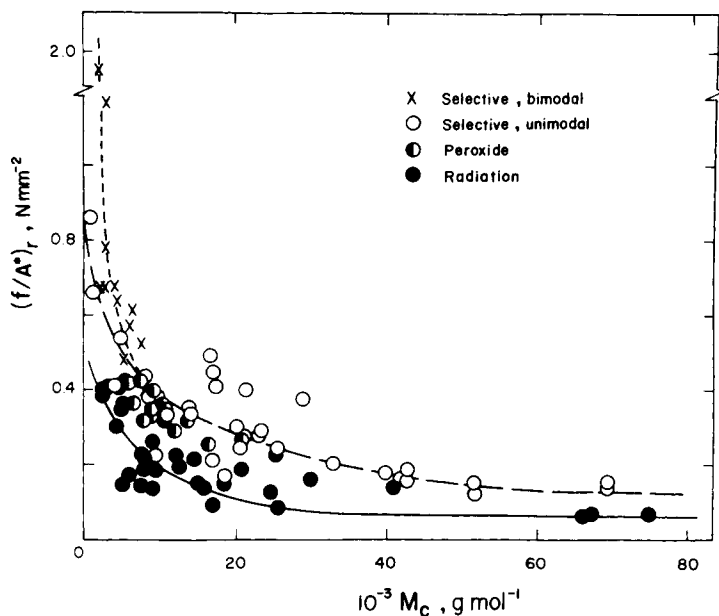
Fig. 2. Values of the ultimate strength (nominal stress at rupture) shown as a function of the approximate molecular weight between cross-links for the same networks described in Figure 1.

network (as estimated from the high-deformation modulus, using a structure factor of one-half).[5,31-34] The largest values of α_r and $(f/A^*)_r$ are obtained for the networks prepared by selectively joining functional groups occurring either as chain ends or as side groups along the chains.[5,8,12,22,23,30] This presumably may be attributed to the relatively low incidence of dangling chains in such networks. (The effects are particularly pronounced when such "model" networks are prepared from a mixture of relatively long and very short chains,[8,12] possibly because the long chains inhibit the growth of rupture nuclei.) Thus, as expected, the lowest values of the ultimate properties generally occur for the networks cured by radiation [ultraviolet (UV) light, high-energy electrons, and γ radiation].[21,26] The peroxide-cured networks, are generally intermediate to these two extremes,[22,23,31] with the ultimate properties possibly depending on whether or not the free-radicals generated by the peroxide are sufficiently reactive to cause some chain scission. These results are at least semiquantitative and certainly interesting, but are somewhat deficient in that information on the number of dangling chains in these networks is generally not available.

The present investigation focuses on a series of model networks prepared by end-linking vinyl-terminated PDMS chains. The tetrafunctional end-linking agent, $Si[OSi(CH_3)_2H]_4$, was used in varying amounts smaller than that corresponding to a stoichiometric balance between its active hydrogen atoms and the chains' terminal vinyl groups. The ultimate properties of these networks, with known numbers of dangling chains, were compared with those obtained on networks previously prepared so as to have negligible numbers of these irregularities.[22,23] In this way it is possible to characterize quantitatively the effects of dangling chains on the ultimate properties of an elastomeric network.

EXPERIMENTAL DETAILS

The polymer employed was part of a Dow Corning PDMS sample which had been used in two previous studies of model networks.[29,30] It had a value of M_n of 11.3×10^3 g mol^{-1}, and at least 95% of the chains had vinyl groups at both ends. Portions of the sample were end-linked into a series of ten networks using $Si[OSi(CH_3)_2H]_4$ in amounts chosen to assure that some of the terminal vinyl groups on the PDMS chains would remain unreacted (and thus produce the desired dangling chains). Concentrations of the chloroplatinic acid catalyst corresponded to 2–4 ppm of elemented Pt, and the reaction conditions and other details were exactly as described previously.[29,30] The relative numbers of dangling chains in each of these predominantly tetrafunctional networks was directly determined by iodometric titration for unreacted vinyl groups;[29,30,35] the results are given in column two of Table I. Values of the volume fraction v_{2C} of polymer incorporated in each of the networks, determined in the usual extraction experiments,[29,30] are given in the following column.

The stress-strain isotherms were obtained on extracted but unswollen strips cut from the various network sheets, using standard techniques,[5,25] at a temperature of 25°C. The strips had cross-sectional areas A^* of approximately 3 mm^2, 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. The elongation was eventually increased to the rupture point of the sample. Since values of the elastic force f were recorded only after they had become sensibly constant, the corresponding values of the modulus and ultimate properties pertain to near-equilibrium conditions.

Equilibrium swelling measurements were carried out on each of the network strips, in benzene at room temperature, as described previously.[5] The extent of swelling was characterized by v_{2m}, the volume fraction of the (already extracted) polymer at equilibrium (maximum) swelling.

TABLE I
Network Structural Characteristics, Elasticity Constants in Elongation, Swelling Equilibrium Results, and Ultimate Properties

Network	Dangling ends (%)	v_{2C}[a]	$2C_1$[b] (N mm^{-2})	$2C_2$[b] (N mm^{-2})	$2C_2/2C_1$	v_{2m}[c]	α_r[d]	$(f/A^*)_r$[e] (N mm^{-2})
1	4.7	0.965	0.196	0.0826	0.421	0.315	1.99	0.411
2	10.8	0.964	0.169	0.115	0.677	0.299	2.00	0.397
3	17.7	—	0.181	0.0874	0.482	0.296	1.70	0.312
4	22.4	0.950	0.130	0.0658	0.506	0.263	2.26	0.330
5	23.4	0.939	0.127	0.0595	0.470	0.265	1.99	0.270
6	23.5	0.950	0.152	0.0818	0.537	0.267	1.63	0.256
7	29.4	0.930	0.146	0.0907	0.623	0.277	2.01	0.341
8	36.2	0.879	0.0606	0.0375	0.619	—	1.59	0.101
9	41.1	0.930	0.0638	0.0315	0.493	0.195	2.32	0.165
10	41.7	0.898	0.0775	0.0311	0.401	0.213	2.37	0.198

[a] Volume fraction of polymer incorporated in the network structure.

[b] Constants in the Mooney-Rivlin representation of the modulus.

[c] Volume fraction of polymer in the network at swelling equilibrium in benzene at room temperature.

[d] Elongation or relative length of the network at rupture.

[e] Nominal stress at rupture.

The PDMS networks used for purposes of comparison had been prepared for use in two previous studies.[22,23] The polymers had been cross-linked through some vinyl side groups, using the same reaction mentioned above. Their values of M_n were quite high (ca. 10^5), and thus the networks formed from them should have negligible proportions of dangling ends. Since they had already been characterized in considerable detail,[22,23] it was necessary only to determine their ultimate properties as already described.

RESULTS AND DISCUSSION

Values of the elastic modulus or reduced stress defined by[5,36–39]

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

were plotted against reciprocal elongation, as suggested by the semi-empirical equation of Mooney and Rivlin

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

in which $2C_1$ and $2C_2$ are constants independent of α.[39–41] Typical isotherms are shown in Figure 3, and demonstrate the fact that the measurements were highly reversible. Least-squares analysis was used on all of the isotherms to obtain values of the elastic constants $2C_1$ and $2C_2$ appearing in eq. (2); the values are given in columns four and five of Table I. The constant $2C_1$ represents the
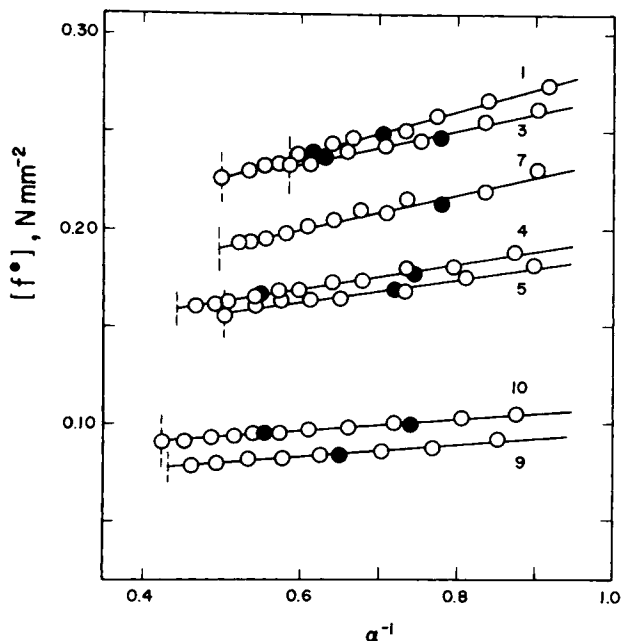

Fig. 3. Typical stress-strain isotherms, in elongation at 25°C, for the (unswollen) PDMS networks. The open circles locate the results gotten using a series of increasing values of the elongation α, the filled circles the results obtained out of sequence to test for reversibility, and the vertical dashed lines the rupture points. Each isotherm was located by least-squares analysis, and is labeled with its identification number from Table I.

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 ($\alpha^{-1} \rightarrow 1$). These moduli are seen to decrease with increase in the proportion of dangling chains; at least for small proportions; however, the decreases are not as large as expected from the predicted dependence[42] of modulus on extent of reaction. As can also be seen from Table I, the ratio $2C_2/2C_1$ of elastic constants does not decrease significantly with increase in the number of dangling chains, as would be expected[39] if these chains acted as diluent "swelling" the network structure. Values of the quantity v_{2m} characterizing the network swelling in benzene are given in column seven of Table I. They show only a small decrease with increase in the number of dangling chains, in agreement with previous observations on polystyrene networks.[17]

Values of the maximum extensibility of the networks are shown as a function of the high deformation modulus $2C_1$ in Figure 4. The networks containing the dangling chains have lower values of α_r, with the largest differences occurring at high proportions of dangling ends (low $2C_1$), as expected. These results thus confirm the less definitive results shown in Figure 1. The values of the ultimate strength are similarly displayed in Figure 5. Again, it is obvious that dangling ends decrease $(f/A^*)_r$, in agreement with the more tentative results presented in Figure 2. [The modulus $[f^*]$ is less sensitive to dangling chains because they cause a decrease in both the numerator and denominator of the defining relationship, Eq. (1).]

It is easiest to visualize these decreases as being due to the dangling chains acting as network irregularities. Part of the decrease could, however, arise from the fact that junctions having one or more dangling chains would have effective functionalities less than the expected value of four. Most junctions would still have four chains emanating from them, either elastically effective or dangling; this effect may therefore be small if it is the degree of entangling around the junction points[32–34] which is of predominant importance in this regard.

As pointed out previously,[7] even more thorough studies of the effects of dangling chains may be carried out by including some monosubstituted chains in
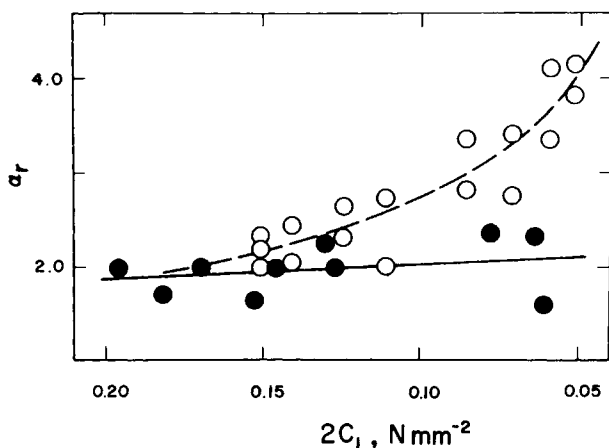

Fig. 4. Maximum extensibility shown as a function of the high deformation modulus $2C_1$ for the PDMS networks containing (i) a negligible number of dangling ends (O) (Refs. 22 and 23) and (ii) the percentages of dangling ends specified in Table I (●). In the latter case, decrease in $2C_1$ corresponds to increase in the number of dangling ends.
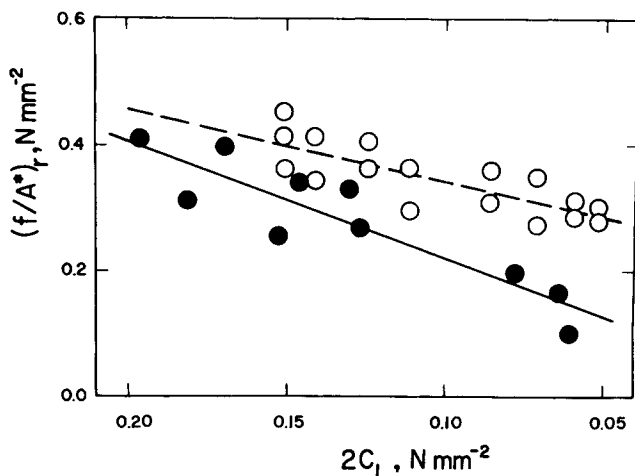
Fig. 5. Ultimate strength for the same networks described in Figure 4.

the preparation of the model networks. In this way it would be possible to vary the lengths of the dangling chains, as well as their relative numbers.

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