The Effect of Chain Length Distribution on Elastomeric Properties. 1. Comparisons between Random and Highly Nonrandom Networks

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Abstract: Two dimethylsiloxane polymers were prepared, both with 0.57 mol % methylvinylsiloxane units. In the first polymer, the potentially reactive vinyl groups were randomly distributed, while in the second they were segregated at the two ends of the chains. Networks were prepared from both polymers, and from various mixtures thereof, using γ-radiation and benzoyl peroxide (which are not selective for vinyl groups), and a silicon hydride cross-linking agent (which is highly selective). They were characterized in terms of their stress-strain isotherms in elongation and their degree of equilibrium swelling in benzene. The networks prepared by selectively cross-linking through the segregated vinyl sites were found to have relatively large values of the molecular weight M_c between cross-links, thus indicating that very short chains have significantly reduced contributions to the elastomeric properties of a network. In effect, two or more closely spaced cross-links act as a single cross-link of higher functionality. The ratio $M_c(f)/M_c(v_{2m})$ of the values of M_c from the stress-strain isotherm and degree of equilibrium swelling was generally found to be close to the expected value of unity. The values of the ratio for the very nonrandom networks suggest, however, that the very short chains contribute even less to the swelling response than they do to the modulus in elongation.

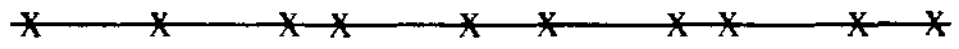
Introduction

When polymer chains of sufficient length and flexibility are cross-linked into a network structure, the resulting material exhibits rubberlike elasticity, i.e., very large and reversible deformability.[2,3] This unique property of a polymeric material has been extensively investigated in a large number of studies, in an attempt to establish the relationships between the elastomeric properties of the network and the details of its molecular structure.[2-17] A great deal of work, for example, is being carried out in order to determine how the modulus of such a network depends on the degree of cross-linking or, equivalently, on the average molecular weight M_c between cross-links ("the molecular weight of a network chain").

Relatively little, however, is known about the effect of the *distribution* of chain lengths on any of the properties of a network. Because of the lack of evidence to the contrary, it is generally assumed that the chain-length distribution has a relatively minor effect on the equilibrium elastic properties of a network. For example, the molecular theories of rubberlike elasticity generally assume that the network chains are all of the same length. Simple molecular arguments, however, suggest how the chain-length distribution can have an important effect. As is well known,[2,3,18] the elastic reponse of a polymer network originates primarily from the decrease in entropy as the network chains are deformed from random spatial configurations to less random ones extended along the direction of deformation. Rubberlike elasticity thus requires that the network chains have a large number of accessible configurations covering a wide range of end-to-end separations. A large number of configurations, in turn, requires relatively long chain length. Thus, for example, chain-length distribution must assume some importance at least to the extent that very short chains should have severely diminished contributions to the elastomeric properties. Also, it is of course conceivable that the chain-length distribution could have rather different effects on different elastomeric properties, for example, the modulus in simple (one-dimensional) elongation and the degree of equilibrium swelling (three-dimensional isotropic dilation). These two properties are of paramount importance in that they are the ones generally used to obtain information on network structure.[2,3]

The above important questions have remained unanswered largely because of the way in which polymer networks have generally been prepared. When the networks are formed in the usual manner,[2,3] i.e., by randomly introducing bonds between chain segments which happen to be in close proximity, irrespective of their positioning along the two polymer chains being joined, it is virtually impossible to control the chain-length distribution. The resulting distribution of cross-links (or of the associated network chain lengths) should be very broad, but there is little quantitative information on the breadth of a typical distribution.

The present study has as its goal the preparation and investigation of networks having relatively well characterized cross-link distributions. The networks were prepared by cross-linking polydimethylsiloxane (PDMS) chains $[Si(CH_3)_2O-]$ containing potentially reactive cross-linking sites, present in known amounts and in known distributions. Specifically, the chains contained 0.57 mol % methylvinylsiloxane units $[Si(CH_3)(CH{=}CH_2)O-]$ either randomly distributed along the chains (i) or segregated at the two ends (ii).



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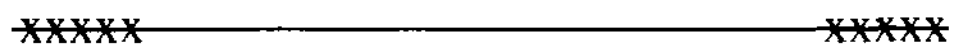

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Both polymers, and mixtures thereof, were cross-linked using γ-radiation, benzoyl peroxide, and $Si[OSi(CH_3)_2H]_4$. The cross-links obtained from the first two techniques should occur essentially nonselectively, thereby yielding a typical random distribution of cross-links irrespective of the structure of the PDMS chains employed. The $Si[OSi(CH_3)_2H]_4$ cross-linking agent, however, should react only with the vinyl groups along the chains, thus permitting close control over the cross-link distribution.

The networks thus obtained were studied with regard to their stress-strain isotherms in elongation and their degree of equilibrium swelling in benzene. Comparisons were carried out so as to characterize the effect of chain-length distribution on the values $M_c(f)$ and $M_c(v_{2m})$ of the molecular weights between cross-links obtained, respectively, from the elongation and the swelling measurements.

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Table I. Cross-Linking Techniques, Polymer Compositions, and Elastomeric Properties of the Resulting Networks

			elongation[a]			swelling[c]		
cross-linking techniques	specificity	fraction F_s of chains with segregated reactive sites	$2C_1$, N mm^{-2}	$2C_2$, N mm^{-2}	$10^{-3}M_c(f)$,[b] g mol^{-1}	v_{2m}[d]	$10^{-3}M_c(v_{2m})$,[b] g mol^{-1}	$M_c(f)/M_c(v_{2m})$
γ-radiation	very low	0.00	0.0870	0.0709	13.8	0.223	16.7	0.826
		0.25	0.0831	0.0627	14.5	0.211	19.3	0.751
		0.75	0.0704	0.0694	17.1	0.212	19.1	0.895
		1.00	0.0586	0.0715	20.5	0.201	21.9	0.936
benzoyl peroxide	very low	0.00	0.1343	0.1359	8.95	0.262	10.5	0.852
		0.25	0.1304	0.1250	9.22	0.260	10.7	0.862
		0.75	0.1134	0.1226	10.6	0.248	12.3	0.862
		1.00	0.1011	0.1232	11.9	0.246	12.6	0.944
$Si[OSi(CH_3)_2H]_4$, Pt catalyst	very high	0.00	0.1108	0.0668	10.9	0.275	9.10	1.20
		0.25	0.0709	0.0707	17.0	0.220	17.3	0.983
		0.75	0.0298	0.0464	40.3	0.156	41.1	0.981
		1.00	0.0282	0.0403	42.6	0.132	59.8	0.712

[a] In the unswollen state, at 25 °C. [b] Molecular weight between cross-links. [c] In benzene, at 25 °C. [d] Volume fraction of polymer in the network at swelling equilibrium.

Experimental Section

Polymer Synthesis. The two dimethylsiloxane polymers used in the study both contained 0.57 mol % methylvinylsiloxane units, as determined by titration[19] with iodine monochloride. This concentration corresponds to an average spacing of $M_c = 13.0 \times 10^3$ g mol^{-1} between vinyl cross-linking sites. The first polymer was prepared by copolymerizing a mixture of dimethyl and methylvinyl cyclic siloxanes using potassium silanolate as equilibrating catalyst to further disperse the vinyl groups along the chain.[20] It had a number-average molecular weight of approximately 3.0×10^5 g mol^{-1}. The other polymer, synthesized and generously provided by A. Ward of the Dow Corning Corp., was polymerized from cyclic siloxane trimer using dianionic "living polymer" techniques[21] to assure that the methylvinylsiloxane units were all located in blocks on the two ends of the chain. Each end had a number-average degree of polymerization of approximately 23 ($M = 1.7 \times 10^3$). Two intermediate degrees of block-like structure or segregation of vinyl units were obtained by mixing various amounts of the two polymers. The chosen values of the fraction F_s of chains in the mixture having the vinyl cross-linking sites located at the ends were 0.25 and 0.75, as well as the limiting values of 0.00 and 1.00.

Network Preparation. The two polymers and the two mixtures were cross-linked using three standard techniques. The samples cross-linked with γ-radiation were first heated under vacuum to remove volatile materials, then sealed into aluminum molds, and exposed to a ^{60}Co source for a time sufficient to provide 1.7 Mrad of radiation to each sample. The samples to be cross-linked with benzoyl peroxide were mixed with 0.5 wt % of the peroxide, volatiles were removed, and the samples were sealed into aluminum molds. They were then cross-linked by heating for 1 h at 125 °C. These two methods are known to involve highly reactive free radicals, and to have very low selectivity for vinyl groups.[22-24] They will, in fact, readily cross-link PDMS chains having no vinyl groups at all.

The samples to be cross-linked by the addition of SiH groups to the $SiCH{=}CH_2$ substituents were also devolatilized and then mixed with sufficient amounts of chloroplatinic acid catalyst and $Si[OSi(CH_3)_2H]_4$ to give 2 ppm elemental platinum by weight and 2 mol of SiH per mol of $SiCH{=}CH_2$. (Using twice the stoichiometric quantity of SiH should give cross-links having an average functionality ϕ of four.) Cross-linking was allowed to proceed for 1 day at 95 °C in open glass dishes. This addition reaction is highly specific for vinyl groups and goes essentially to completion with no side reactions, byproducts, or isomerization.[14,25]

All of the networks were extracted using benzene; the soluble material thus removed amounted to only approximately 5%, and was presumably inert cyclics.

Elasticity Measurements. The stress–strain isotherms were obtained on strips cut from the dried (unswollen) networks, at 25 °C, in the usual manner.[13,26,27] The cross-sectional areas A^* of the strips were measured by micrometer, and the lengths L of the central test portions of the strips by a cathetometer. The elastic force f was measured using a standard stress gauge,[13,26,27] and was recorded only after it became sensibly constant. Stress–strain measurements were made using a sequence of increasing values of the elongation (relative length) of the sample $\alpha = L/L_i$, with frequent inclusions of values out of sequence to test for reversibility.

Equilibrium swelling measurements were also carried out on each strip, in benzene at 25 °C, as described previously.[13] The degree of swelling was characterized by v_{2m}, the volume fraction of polymer at equilibrium (maximal) swelling. It was calculated assuming simple additivity of volumes of PDMS network and benzene swelling agent.

Results and Discussion

The stress–strain data were interpreted in terms of the "reduced stress" or modulus defined by[13,28-30]

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

The equilibrium values of $[f^*]$ were plotted against reciprocal elongation, as suggested by the semiempirical equation of Mooney and Rivlin[3,31]

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

in which $2C_1$ and $2C_2$ are constants independent of α. Some typical stress–strain isotherms, thus represented, are shown in Figure 1. Least-squares analysis was used to locate the best lines through these and the other isotherms. The results obtained upon decreasing α are seen to be in excellent agreement with those obtained during the main sequence of increasing values of α, thus demonstrating the reversibility of the isotherms. The values of the constants $2C_1$ and $2C_2$ characterizing each isotherm are given in columns 4 and 5 of Table I. According to the most recent theories of rubberlike elasticity,[6,8,10,11] the ratio $2C_2/2C_1$ is a measure of the extent to which the elastic deformation changes from affine to nonaffine with increasing stress, and is thus related to the looseness with which the cross-links are embedded within the network structure. The present results yield $2C_2/2C_1 = 1.05$ (±0.20), which is in excellent agreement with the theoretically predicted value of unity for a tetrafunctional network.[8,10]

The values of $2C_1$ were used to calculate stress–strain values $M_c(f)$ of the molecular weight between cross-links, by means of the equation[8,10,13]

$$M_c(f) = A_4\rho kT/2C_1 \qquad (3)$$

in which ρ is the density of the network and kT is the product of the Boltzmann constant and the absolute temperature, 298.2 K. According to theory,[8,10] the structure factor A_ϕ is given by $1 - 2/\phi$, and should thus have the value of one-half in the case of a tetrafunctional network. Values of $M_c(f)$ thus calculated

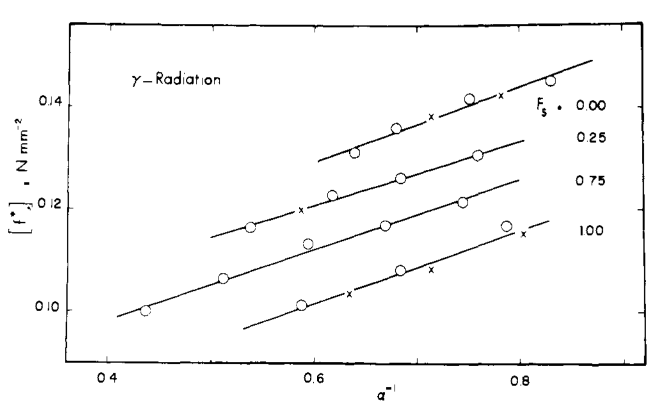

Figure 1. Typical stress-strain isotherms obtained on the PDMS networks in the unswollen state, in elongation at 25 °C. The data shown pertain to networks obtained by cross-linking mixtures of PDMS chains by means of γ-radiation. The fraction of chains in the mixture which had the cross-linking sites segregated at the chain ends is specified for each isotherm. The open circles pertain to data obtained using a sequence of increasing values of the elongation α, and the X's to data taken out of sequence to check for reversibility.

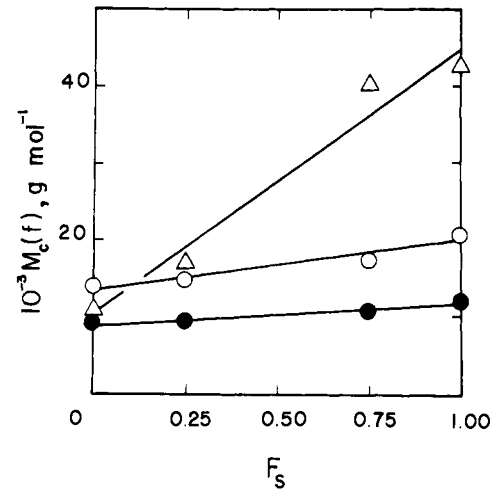

Figure 2. Values of the molecular weight M_c between cross-links, as calculated from the stress-strain isotherms, for all of the PDMS networks. The results are shown as a function of the fraction of chains having the cross-linking sites segregated at the ends of the chains. The three types of networks were prepared by γ-radiation (○), benzoyl peroxide (●), and $Si[OSi(CH_3)_2H]_4$ (△).

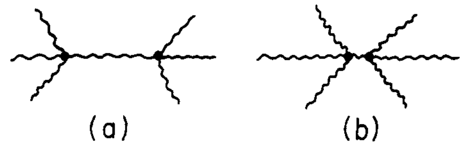

Figure 3. A schematic illustration of the effect of cross-link spacing. Part (a) illustrates two randomly spaced tetrafunctional cross-links. In part (b), the chain joining the two cross-links is so short that it is elastically ineffective, thus causing the two cross-links to act as a single cross-link of functionality six.

are given in column 6 of Table I. The result presented in row 9 is of particular importance since, in this selectively cross-linked network, the only cross-links should be at the vinyl sites and these should be randomly located ($F_s = 0$) along the chains. The observed value $10^{-3}M_c(f) = 10.9$ is in good agreement with the value 13.0 expected from the average spacing of the vinyl groups, as described in the Experimental Section. Revision of A_4 from 0.50 to the experimental value 0.65 obtained in a study of tetrafunctionally end-linked model PDMS networks[13] would yield $10^{-3}M_c(f) = 14.2$. The close agreement among these results strongly indicates that the $Si[OSi(CH_3)_2H]_4$ cross-linking reaction does go essentially to completion.

The values of $M_c(f)$ are shown as a function of the degree F_s of vinyl site segregation in Figure 2. The networks prepared by γ-radiation and by benzoyl peroxide show only a slight increase in $M_c(f)$ with F_s, whereas the networks prepared using the $Si[OSi(CH_3)_2H]_4$ reaction show a very much larger increase. These results are readily interpreted by noting that $M_c(f)$ is directly proportional to the structure factor but inversely proportional to the number of elastically effective chains, i.e., $M_c(f) \propto (1 - 2/\phi)N^{-1}$. If the spacing between two cross-links becomes too small, as is illustrated in Figure 3, the intervening chain must become elastically rather ineffective, and the two cross-links act approximately as a single cross-link of higher functionality. As is evident from the form of the product $(1 - 2/\phi)N^{-1}$, the increase in ϕ is not sufficient to offset the decrease in N, and $M_c(f)$ increases correspondingly. Thus the results in Figure 2 strikingly confirm the expectations that (1) the selectivity of γ-radiation and benzoyl peroxide is very low, (2) the selectivity of the $Si[OSi(CH_3)_2H]_4$ cross-linking agent is very high,[32] and (3) the chain-length distribution can have a significant effect on the elastomeric properties of a network.

The values of the volume fraction v_{2m} of polymer in each of the networks at swelling equilibrium in benzene at 25 °C are given in column 7 of Table I. They were interpreted in terms of the classic swelling equation[2,13,26]

$$M_c(v_{2m}) = -A_4\rho V_1 v_{2m}^{1/3}/[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2] \qquad (4)$$

in which $V_1 = 89.86$ cm^3 mol^{-1} is the molar volume of the benzene and χ_1 is the free energy of interaction parameter[2] between the benzene and the PDMS networks. The required values of χ_1 were obtained from published results,[30] which indicate $\chi_1 = 0.484 + 0.330v_{2m}$ for the pertinent range of v_{2m}; the values thus obtained ranged from 0.528 to 0.575. The resulting values of $M_c(v_{2m})$ are given in column 8 of Table I. There is, unfortunately, a rather large uncertainty in these results because there is some uncertainty with regard to the exact form of the swelling equation,[11,27,33] and the results obtained are very sensitive[34] to the interaction parameter χ_1.[35] In any case, it should still be useful to compare values of $M_c(f)$ and $M_c(v_{2m})$, and values of their ratio $M_c(f)/M_c(v_{2m})$ are given in the final column of Table I. The results for the networks prepared by γ-radiation and by benzoyl peroxide are all close to the expected value of unity, with no obvious dependence on the degree of segregation F_s of the vinyl groups. In the case of the networks selectively cross-linked by the $Si[OSi(CH_3)_2H]_4$, however, there does appear to be a significant decrease in this ratio with increasing F_s, suggesting that the very short chains contribute even less to the swelling response than they do to the modulus in elongation. Although the observed change is not much larger than the uncertainty in some of the swelling results, it is much larger than the change observed for the same range of M_c in the case of end-linked PDMS networks of relatively narrow distribution.[13] This dependence persists, and is sometimes of much larger magnitude, for alternative ways of interpreting the elongation and swelling results,[34,35] including the most recent theory of swelling equilibrium.[11] Although much more experimental data will be required to provide a definitive answer to this problem, the present results do suggest that the chain-length distribution could have different effects on the different properties used to characterize network structures.

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Dependence of Bond Angles upon the Steric Effect. 1. XMX Bond Angles

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Abstract: Bond angles X–M–X in tetrahedral and trigonal planar species are generally dependent on steric effects. This is shown by the success of correlations with the equation $1/\sin(\theta_X/2) = b_0(1/r_{VX}) + b_1$, where $\theta_X = \angle XMX$ and r_{VX} is the van der Waals radius of X, and $1/\sin(\theta_X/2) = d_1 r_{VM} + d_0$, where r_{VM} is the van der Waals radius of M. The correlation equations are useful for the prediction of bond angles. H atoms bonded to O, N, or C do not fit the steric effect model. Groups X capable of $d\pi$–$p\pi$ bonding also do not fit the model.

The valence shell electron pair repulsion (VSEPR) theory has been very widely used in the prediction of the shape of a chemical species on the basis of repulsions between electron pairs.[1] The theory does not successfully account for the deviation of the observed bond angles in many compounds from the predicted geometry. These deviations, although small, are experimentally significant. According to VSEPR theory, they are due to the electronegativity of the substituents attached to the central atom. Searcy has attempted to predict bond angles from an electrostatic model.[2]

An alternative viewpoint has been presented[3] which suggests that in many cases the observed bond angles can be accounted for by interactions between nonbonded atoms. This proposal has been criticized by Wilson[4] on the grounds that equally good predictions in the case of trigonal planar carbon compounds could be made by simply assuming average values for the bond angles. Nonbonded interactions have been used recently to account for the geometry of a number of species. In this work we present evidence based on a very simple model which suggests that generally bond angles are determined by steric effects (nonbonded atom repulsions).

Consider the structural fragment X^1–M–X^2 shown in Figure 1, where $X^1 = X^2$, X is some atom or group of atoms, and M is a central atom to which the two X groups are bonded. If the bond angle is determined by the size of the X group, the two X groups will be in contact, and the distance $\overline{XA}$ from the X nucleus to the point A at which the X groups are in contact will be equal to the van der Waals radius of X if X is monatomic. If X is polyatomic, the distance $\overline{XA}$ will be from the group center to the point in contact and will be given by the group van der Waals radius, r_{VX}. The distance $\overline{XM}$ is simply the XM bond length. As triangles X^1AM and X^2AM are congruent, angle X^2MA is equal to angle X^1MA and designating angle X^1MX^2 as θ

$$X^1MA = \theta_X/2 \tag{1}$$

Then

$$r_{VX} = l_{MX} \sin(\theta_X/2) \tag{2}$$

$$1/\sin(\theta_X/2) = l_{MX}/r_{VX} \tag{3}$$

We may write

$$l_{MX} = r_{CM} + r_{CX} \tag{4}$$

where r_{CM} and r_{CX} are the covalent radii of M and X, respectively. We have shown elsewhere[5] that as suggested by

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