$$\langle \cos^2 \theta \rangle = \frac{1}{2\pi}\int_0^{2\pi} \cos^2 \theta \, d\theta \qquad (16)$$

In measuring $R_z^{\perp}$ the equation to be used is:

$$I(\kappa) = I(0) \exp[-\kappa^2 (R_z^{\perp})^2/2] \qquad (17)$$

Similarly for $R_2^{\parallel}$, if we have complete orientation:

$$I(\kappa) = I(0) \exp[-\kappa^2 (R_z^{\parallel})^2] \qquad (18)$$

However, in the samples discussed in Table II orientation was not complete and our principal discussion relates to values of $R_z^{\perp}$. However, approximate values of $R_z^{\parallel}$ obtained by curve fitting of data derived from measurements parallel to the drawing axis, using known values of M_w to fix the value of the intercept, led to the conclusion that $(R_z^{\parallel}/R_z^{\perp}) \simeq 3$. One explanation for the results in Table II is that the molecules have separated into discrete domains with molecular weights $(M_w^{\perp})$ in the region 32000–55000. These domains are connected by fragments of the macromolecule which are too few in number to contribute significantly to the scattering at right angles to the direction of drawing. It is due to the lower limit of κ accessible to the Julich spectrometer that, for these highly anisotropic scatterers, one obtains the molecular weight of the separated fragment of the macromolecule. Similarly values of $R_z^{\perp}$ give information of the total cross section of the molecules contained within these domains.

Etching experiments[2] show that only discrete lamellae are present with similar d spacing to that measured in the undrawn samples. A possible model consistent with the data obtained for sample OPP2 is that the molecule is folded between four lamellae as shown in Figure 7. Each lamellae contains 10 or more stems and these are connected by 2 to 3 tie fragments. This supports the observation made on the isotropic system that a macromolecule in crystalline polymers can inhabit more than one lamellae. The values of $R_z^{\perp}$ also give information concerning the average distance between stems. Adjacent re-entry or close packing of the stems would lead to a value of $R_z^{\perp}$ approximately a quarter of the value observed. It is concluded from these measurements therefore that the stems are widely spaced either separately or in pairs of undetermined distance apart.

It should be noted that etching gives values for the stem length close to the SAXS value for the d spacing and only one stem was identified in the etching system. Similar studies on biaxially oriented polypropylene show only the presence of one stem, and this also is equal in length to the SAXS value of the d spacing.

It is interesting to compare the Kratky plot at right angles to the direction of drawing (Figure 6) with that of isotropic polypropylene shown in Figure 4. The unusual feature is that the asymptotic value for the Kratky function, $I\kappa^2$ where $I = \mathrm{d}\sum(\kappa)/\mathrm{d}\Omega$, is nearly twice the value observed for the isotropic polymer. The reasons for this are not clear and more drawn systems need to be studied. It may not be due to the anisotropy of the system but to the fact that the molecule has contracted in this direction.

Finally, a comparison of the structure of the isotropic quenched polymer with the cold drawn samples shows that the latter is not merely an extension of the former. In fact the molecule has undergone a large reorganization in which some of the original lamellae have been fractured.

References and Notes

(1) D. G. H. Ballard, J. Schelten, P. Cheshire, and G. W. Longman, *Polymer*, **19**, 379 (1978).
(2) D. G. H. Ballard, J. Schelten, T. L. Crowley, and G. W. Longman, *Polymer*, **20**, 399 (1979).
(3) J. Schelten, D. G. H. Ballard, G. D. Wignall, G. W. Longman, and W. Schmatz, *Polymer*, **17**, 754 (1976).
(4) Yoon and Flory, *Faraday Discuss.* (Sept. 1979).
(5) C. Picot, R. Duplessix, D. Decker, H. Benoit, F. Boue, J. P. Cotton, M. Daoud, B. Farnoux, G. Jannink, M. Nierlich, A. J. de Vries, and P. Pincus, *Macromolecules*, **10**, 436 (1977).

Model Networks of End-Linked Poly(dimethylsiloxane) Chains. 8. Networks Having Cross-Links of Very High Functionality[‡]

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ABSTRACT: Elastomeric networks were prepared from poly(dimethylsiloxane) chains having vinyl groups at both ends. The chains were end-linked with the use of a series of cross-linking agents, including some containing a large number of reactive $Si(CH_3)H$ groups. The resulting networks had values of the cross-link functionality ϕ covering the approximate range 3–37. They were studied with regard to their stress–strain isotherms in elongation at 25 °C and their degree of equilibrium swelling in benzene at room temperature. The values of the modulus in the limits of large and small deformations, the degrees of equilibrium swelling, and the dependence of these properties on ϕ were found to be in satisfactory agreement with the recent molecular theory developed by Flory. The elastic constant $2C_2$, which characterizes the dependence of the modulus on elongation, was found to approach zero as ϕ increased to very large values. This important result is also in agreement with the Flory theory, which interprets the decrease in modulus with an increase in elongation as resulting from a continuous change from a nearly affine deformation to the highly nonaffine deformation characteristic of a "phantom" network.

Elastomeric networks consist of chain molecules joined at junctions (cross-links) which have a functionality ϕ of three or higher. As would be expected, the elastomeric properties of such materials strongly depend on the number density of such junctions in the network or, equivalently, on the average molecular weight between such junctions. There have, in fact, been an exceedingly large number of studies addressed to the problem of relating elastomeric properties such as the elongation modulus or equilibrium degree of swelling to this particular structural feature of a polymer network.[1,2]

In contrast, relatively little is known about the dependence of the elastomeric properties of a network on the *functionality* of its junction points. The desired relationships have been predicted in a number of molecular

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[‡] It is a particular pleasure to dedicate this paper to Professor Paul J. Flory on the occasion of his 70th birthday.

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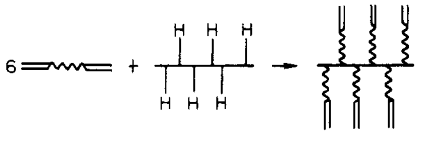
Table I
Preparative Conditions and Stress–Strain and Swelling Equilibrium Results for the PDMS Networks

end-linking agent[a]	ϕ	reaction conditions: days; °C	v_{2C}[b]	$2C_1$, N mm^{-2}	$2C_2$, N mm^{-2}	A_ϕ	A_ϕ'	v_{2m}[c]
A	3.0	2; 70	0.967	0.183	0.0918	0.88	1.32	0.312
A	3.0	1; 95	0.965	0.178	0.0976	0.85	1.32	0.311
A	3.0	1; 95	0.966	0.165	0.120	0.79	1.37	0.306
A	4.0	2; 70	0.965	0.196	0.0826	0.94	1.34	0.315
A	4.0	1; 95	0.964	0.169	0.115	0.82	1.37	0.299
B	4.0	1; 95	0.966	0.199	0.0759	0.96	1.32	0.330
B	4.6	1; 95	0.961	0.217	0.0776	1.05	1.42	0.310
B	5.0	1; 95		0.217	0.0661	1.07	1.39	0.322
B	5.0	1; 95	0.956	0.179	0.0454	0.87	1.09	0.293
B	5.0	2; 70	0.963	0.226	0.0419	1.09	1.29	0.314
A-C-A	6.0	2; 70	0.965	0.241	0.0572	1.16	1.43	0.319
				0.239	0.0559	1.15	1.39	0.319
B-C-B	8.0	2; 70	0.965	0.277	0.0195	1.33	1.43	0.342
				0.271	0.0275	1.30	1.43	0.338
B-C-B-C-B	11	2; 70	0.967	0.287	0.0111	1.38	1.44	0.346
				0.294	0.0129	1.42	1.48	0.350
D	37	1; 95	0.939	0.232	0.0078	1.14	1.17	0.323
D	37	1; 95	0.950	0.231	0.0396	1.12	1.32	0.321
D	37	2; 70	0.952	0.225	0.0128	1.09	1.16	0.304

[a] A, $Si[OSi(CH_3)_2H]_4$; B, cyclic $[OSi(CH_3)H]_5$; C, $O[Si(CH_3)_2CH{=}CH_2]_2$; D, $(CH_3)_3Si[OSi(CH_3)H]_{37}OSi(CH_3)_3$. [b] Volume fraction of polymer successfully incorporated in the network structure. [c] Volume fraction of polymer in the network at swelling equilibrium in benzene at room temperature.

theories of rubberlike elasticity,[3-7] but there are very few experimental results suitable for comparing theory and experiment. The reason resides in the methods almost invariably used to prepare elastomeric networks. They involve the random joining of a pair of segments along two chain molecules, and thus almost invariably lead to junctions of functionality four. The capability of varying the junction functionality therefore requires the use of much more specific, highly controllable chemical reactions, the most useful of which involves joining chains exclusively (and exhaustively) at their ends. Very important examples of such networks are those formed from poly(dimethylsiloxane) (PDMS) chains having hydroxyl groups at both ends end-linked with tetraalkoxy and trialkoxy silanes.[8-15] Tetrafunctional and trifunctional PDMS networks thus prepared have been investigated[8-15] and were found to give results in support of theoretical predictions.[3-5] It is very difficult, however, to extend this particular chemical reaction to include other (higher) network functionalities, which is of course necessary to provide a more definitive test of theory.

The present investigation involves a related but more versatile elastomeric system.[16-21] The PDMS chains have vinyl groups at both ends and yield networks of any functionality ϕ by reaction with any of a variety of siloxane molecules having ϕ (relatively closely spaced) active hydrogen atoms. For example, a hexafunctional network would be prepared by the schematic reaction



(1)

where =ʌʌʌ= represents a vinyl-capped PDMS chain. In this way, a number of end-linking agents were used, with PDMS chains of constant molecular weight, to prepare networks having functionalities ranging from 3 to 37. They were studied with regard to their values of the elongation modulus in the limits of large and small deformations and their degrees of equilibrium swelling in benzene at room temperature. The experimental results thus obtained were then compared with theoretical predictions[3-7] of the effect of junction functionality on these elastomeric properties.

Experimental Section

All of the networks were prepared from the same polymer, an unfractionated sample of PDMS. According to GPC and chemical analysis, it had a number-average molecular weight M_n of 11.3 × 10^3 g mol^{-1} and vinyl groups at both ends of at least 95% of the chains.[22,23] The four end-linking reactants were A ($Si[OSi(CH_3)_2H]_4$), B (cyclic $[OSi(CH_3)H]_5$), C ($O[Si(CH_3)_2CH{=}CH_2]_2$), and D ($(CH_3)_3Si[OSi(CH_3)H]_{37}OSi(CH_3)_3$). All were of high purity except D which, because of its relatively high degree of polymerization, had a polydispersity index the order of 2. All were characterized with regard to structure and reactivity with the use of standard chemical titration techniques.[22,23] The use of A, B, and D in amounts giving equal numbers of active Si–H groups and PDMS vinyl end groups gave networks having functionalities of ϕ = 4, 5, and 37, respectively. Networks having average values of ϕ of approximately 3, 4, and 4.5 were obtained by using more than these equivalent amounts of A, B, and D, respectively. An average functionality of 6 or 8 was obtained by first coupling two molecules of A or B through a molecule of divinyl compound C and a functionality of approximately 11 by first coupling 3 molecules of B with 2 of C. This information is summarized in the first two columns of Table I.

The coupling reactions used to increase the functionality of the end-linking agents were carried out in sealed flasks, at 70 °C, for a period of 1 day. Chloroplatinic acid was used as the catalyst and was present in an amount corresponding to 10 ppm of elemental Pt relative to the total weight of reactants. The polymer end-linking reactions were carried out in a similar manner in aluminum molds under a nitrogen atmosphere, using the equivalent of 2 ppm of the elemental Pt. The reactions were allowed to proceed, in the absence of diluent, for either 2 days at 70 °C or for 1 day at 95 °C, as is summarized in the third column of the table. The resulting networks were extracted in benzene for 4 days, deswelled in benzene–methanol mixtures, and then dried. Gel contents, expressed in terms of the volume fraction v_{2C} of polymer successfully incorporated in the network structure, are given in column four. Sol contents ($1 - v_{2C}$) amounted to approximately 4% and presumably were due to the small amount of inert species known to be present in the types of reactants employed.

The stress–strain isotherms were obtained on strips cut from the dried (unswollen) networks, at 25 °C, in the usual manner.[8,10,11,24] Stress–strain measurements were made with the use of a sequence of increasing values of the elongation or relative length of the sample $\alpha = L/L_i$, with frequent inclusions of values

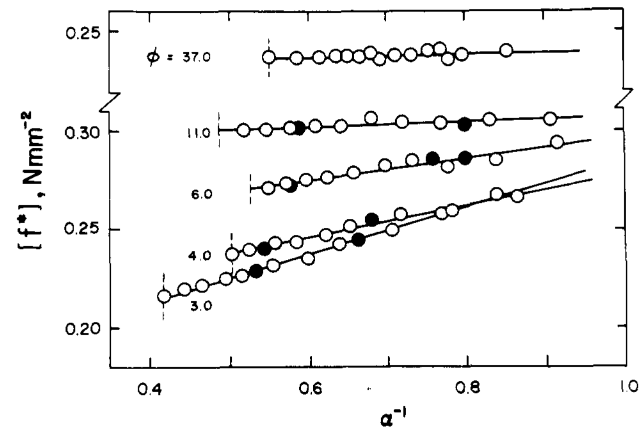


Figure 1. Representative stress-strain isotherms for the end-linked PDMS networks, in elongation at 25 °C. Each isotherm shown is labeled with the functionality ϕ of the network junctions or cross-links, and all isotherms were located with the use of least-squares analysis. The vertical dotted lines show the values of the elongation α at which rupture occurred. The open circles locate the results obtained with the use of a series of increasing values of α, and the filled circles indicate the results obtained out of sequence to test for reversibility.

out of sequence to test for reversibility. Entire stress-strain isotherms were frequently repeated two or three times. In some cases, an entirely new network was prepared, and these duplicate runs thus serve as tests primarily of the reproducibility of the synthetic techniques employed. In other cases, different strips were cut from the same network sheet, thus providing a test primarily of the stress-strain measuring techniques.

Equilibrium swelling measurements were carried out on each of the network strips, in benzene at room temperature, as described previously.[8] The extent of swelling was characterized by v_{2m}, the volume fraction of polymer at maximum swelling, which was calculated by assuming simple additivity of volumes.

Results and Discussion

The stress-strain data were interpreted in terms of the "reduced stress" or modulus defined by[8,24-26]

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

where f is the equilibrium value of the elastic force and A^* is the cross-sectional area of the undeformed sample. The values of $[f^*]$ were plotted against reciprocal elongation, as suggested by the semiempirical equation of Mooney and Rivlin[27]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \tag{3}$$

in which $2C_1$ and $2C_2$ are constants independent of α. Thus the value of the modulus is $2C_1$ in the limit at large deformation ($\alpha^{-1} \to 0$) and $2C_1 + 2C_2$ in the limit at small deformation ($\alpha^{-1} \to 1$). Typical stress-strain isotherms, thus represented, are shown in Figure 1. 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 five and six of the table. As can be seen from the sets of values of $2C_1$ and $2C_2$ listed in the table, there was a high degree of reproducibility in the end-linking techniques used to synthesize the networks, with no significant difference between the 1-day and 2-day cures. There was also good reproducibility in the techniques used to determine the values of the equilibrium stress and strain in the elongated networks.

According to the new Flory theory of rubber-like elasticity,[3-5] the elasticity constant $2C_1$ should be proportional to the factor $(1 - 2/\phi)$. It should therefore increase with ϕ, reaching an asymptotic limit at three times the value pertaining to the minimum functionality of $\phi = 3$. The relevant experimental results are shown in the uppermost portion of Figure 2. They qualitatively follow this trend, except for the networks of highest functionality, which may be incompletely end-linked because of possible steric difficulties in having 37 chains terminate within a relatively small volume. Nonetheless, these networks must have junctions of unusually high functionality and are therefore of considerable importance with regard to the effect of ϕ on the other elasticity constant.

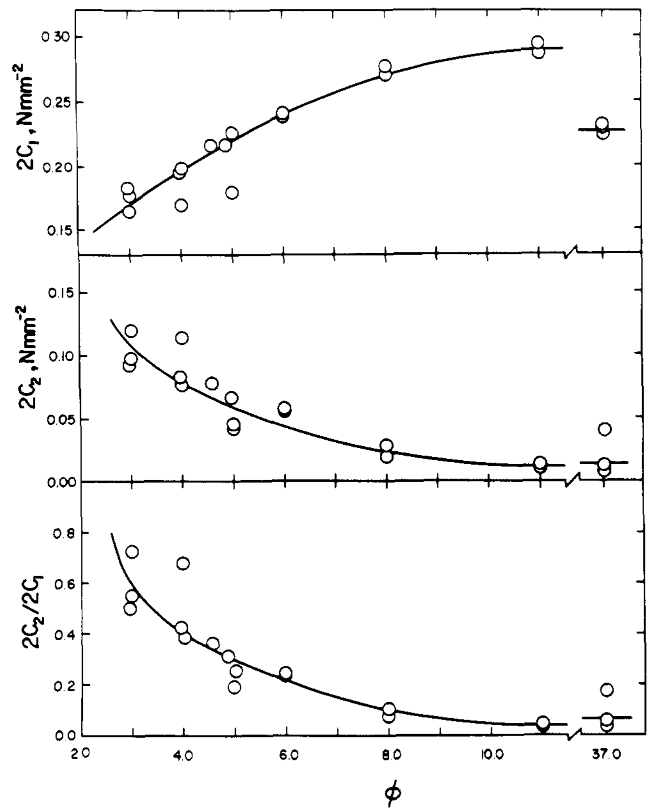


Figure 2. The dependence of the elasticity constants $2C_1$ and $2C_2$ and their ratio $2C_2/2C_1$ on the cross-link functionality.

As shown in eq 3, this other constant, $2C_2$, is a measure of the decrease in modulus as the elongation increases without limit. The decrease is viewed[3,4,28] as arising from the deformation changing from an essentially affine one to the markedly nonaffine one characteristic of a "phantom" network. Junctions of higher functionality will be more firmly embedded within the network structure and such networks should therefore have moduli which decrease less with increasing elongation, i.e., $2C_2$ should be smaller. In the limit of very high ϕ, the deformation should remain essentially affine at all deformations, and $2C_2$ is therefore predicted to approach zero. The pertinent experimental results, $2C_2$ and $2C_2/2C_1$ plotted against the functionality, are shown in the two lower portions of Figure 2. Although there is some scatter in these experimental results, they are obviously in good agreement with the theoretical predictions.

The elongation results were more quantitatively interpreted in terms of the "structure factors" relating the elasticity constants to the average molecular weight of the network chains. Specifically, the values of $2C_1$ listed in the table were interpreted with the use of the equation[3,4,11,13]

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

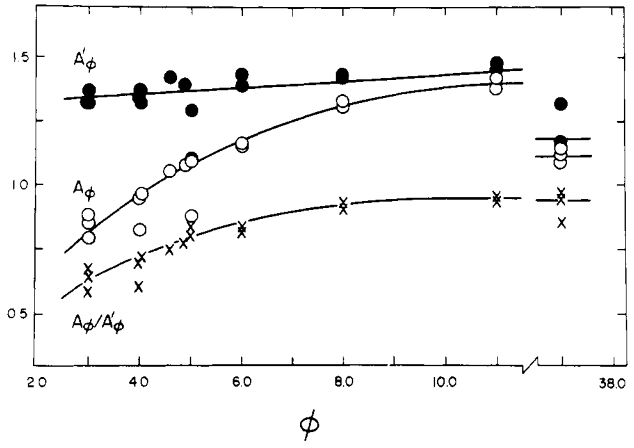


Figure 3. The dependence of the structure factors A_ϕ and A_ϕ' and their ratio A_ϕ/A_ϕ' on the cross-link functionality.

in which A_ϕ is the "structure factor" for the ϕ-functional network, ρ is the density of the network, k is the Boltzmann constant, and $T = 298.2$ K is the absolute temperature. The average molecular weight M_c between cross-links in the network (i.e., the molecular weight of the network chains) has been taken to be M_n of the PDMS chains prior to their cross-linking, because of the nature and near-completeness of the end-linking reaction.[16-20,29] Since $2C_1$ represents the modulus in the limit of large elongation, the deformation should be nonaffine, to an extent dependent on ϕ. Specifically, A_ϕ is predicted to be equal to $1 - 2/\phi$.[3,4,6,7] The experimental values of ϕ thus calculated are given in column seven of the table and are shown as a function of ϕ in Figure 3. In the case of the networks having the minimum values 3 and 4 of the functionality, it is possible to compare the present results with those obtained in some previous studies. (Additional comparisons between various results reported in the literature have been given by Mark and co-workers[8,10,11,19] and by Flory.[30]) The present values of A_3 average to 0.84 (±0.03), which is larger than the value 0.54 (±0.11) reported by Mark and Llorente for networks prepared by trifunctionally end-linking hydroxyl-terminated PDMS chains.[13] The discrepancy may simply be due to the serious experimental difficulties involved in making perfect networks of either type. The average value found for A_4 is 0.91 (±0.06), which is in good agreement with the previous results of 0.81 (±0.16) for hydroxyl-terminated PDMS networks.[11,13] In any case, these networks exhibit values of A_3 and A_4 significantly larger than the expected values of $^1/_3$ and $^1/_2$.[3,4] This suggests that the deformation may not become nonaffine to the extent which would be exhibited by a "phantom network".[3,4] It is important to note, however, that A_ϕ does increase and then level off with increasing ϕ, as predicted by theory.

It is also useful to interpret the modulus in the limit of small deformation since a much shorter extrapolation of the experimental data is required. One disadvantage, however, is the fact that $2C_1 + 2C_2$ slightly over-estimates this limiting value of the modulus because of the nonlinear leveling off of the modulus as the elongation decreases toward unity.[4,31,32] In any case, in this region the deformation should be nearly affine for networks of any functionality and the factor A_ϕ' defined by

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

should always be equal to unity.[3,4,30] The observed values of A_ϕ' are given in column eight of the table and are shown as a function of ϕ in Figure 3. The average value of A_3' is 1.34 (±0.02), which is somewhat larger than the value of 1.02 (±0.27) reported previously.[13] The corresponding value of A_4' is also 1.34 (±0.02), in excellent agreement with the previous result, 1.29 (±0.36).[11,13] These values are somewhat larger than the predicted value of unity,[3,4] but significantly smaller than the values reported for A_3' and A_4' by Valles and Macosko.[18] In any case, the present results are in excellent agreement with the prediction that A_ϕ' be relatively independent of ϕ. The ratio A_ϕ/A_ϕ' is predicted to be 1/3 at $\phi = 3$ and to reach an asymptotic value of unity in the limit of large ϕ. The experimental values, also shown in Figure 3, are in good agreement with this prediction.[33]

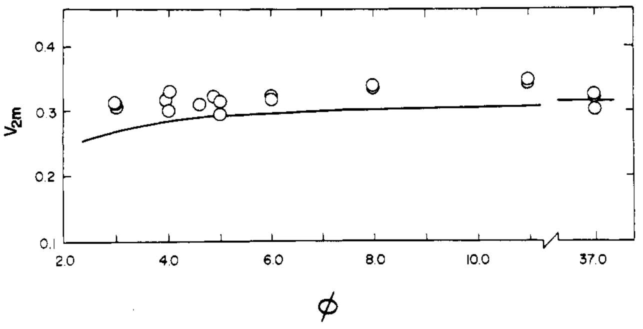


Figure 4. The volume fraction of polymer at equilibrium (maximum) swelling in benzene at room temperature shown plotted against the cross-link functionality. The circles correspond to the present experimental results and the curve represents the prediction of the new Flory theory of network swelling.[5]

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 the table and are shown as a function of ϕ in Figure 4. The interpretation of the swelling results utilized the very recent theory of Flory,[5] in which the extent to which the deformation is nonaffine depends on the looseness with which the junctions or 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. In this case, comparisons between theory and experiment are most conveniently carried out in terms of the generalized swelling equation resulting from the use of eq 12 of ref 5 for the elastic free energy of deformation. The result is

$$M_c = -F_\phi \rho V_1 v_{2C}^{2/3} v_{2m}^{1/3} / [\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2] \qquad (6)$$

in which F_ϕ is a factor characterizing the extent to which the deformation in swelling approaches the affine limit, $V_1 = 89.08$ cm^3 mol^{-1} is the molar volume of the benzene, and χ_1 is the free energy of the interaction parameter[1] between the benzene and the PDMS networks. The required values of χ_1 were obtained from published results,[25] which indicate $\chi_1 = 0.484 + 0.330 v_{2m}$ for the pertinent range of v_{2m}. The theoretical values of F_ϕ are given by

$$F_\phi = (1 - 2/\phi)[1 + (\mu/\xi)K] \qquad (7)$$

where μ is the number of junctions and ξ is the cycle rank of the network. For a perfect ϕ-functional network, μ/ξ is equal to $2/(\phi - 2)$.[5] 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 $\kappa = 20$.[5,11,13,15] All of this information was used in eq 6 to calculate predicted values of v_{2m} as a function of ϕ. The results are shown by the curve in Figure 4. The Flory swelling theory is seen to be very successful in that it predicts v_{2m} to be only slightly dependent on junction functionality and to have a value quite close to that obtained experimentally.

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References and Notes

(1) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, New York, 1953.
(2) Treloar, L. R. G. "The Physics of Rubber Elasticity", 3rd ed.; Clarendon: Oxford, 1975.
(3) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1976**, 351, 351.
(4) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(5) Flory, P. J. *Macromolecules* **1979**, *12*, 119.
(6) Duiser, J. A.; Staverman, A. J. In "Physics of Non-Crystalline Solids"; Prins, J. A., Ed.; North Holland: Amsterdam, 1965.
(7) Graessley, W. W. *Macromolecules* **1975**, *8*, 186, 865.
(8) Mark, J. E.; Sullivan J. L. *J. Chem. Phys.* **1977**, *66*, 1006.
(9) Sullivan, J. L.; Mark, J. E.; Hampton, P. G., Jr.; Cohen, R. E. *J. Chem. Phys.* **1978**, *68*, 2010.
(10) Mark, J. E.; Rahalkar, R. R.; Sullivan, J. L. *J. Chem. Phys.* **1979**, *70*, 1794.
(11) Llorente, M. A.; Mark, J. E. *J. Chem. Phys.* **1979**, *71*, 682.
(12) Mark, J. E. *Makromol. Chem., Suppl. 2* **1979**, *180*, 87.
(13) Mark, J. E.; Llorente, M. A. *J. Am. Chem. Soc.*, **1980**, *102*, 632.
(14) Llorente, M. A.; Mark, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 181.
(15) Andrady, A. L.; Llorente, M. A.; Mark, J. E. *J. Chem. Phys.* **1980**, *72*, 2282.
(16) Valles, E. M.; Macosko, C. W. *Rubber Chem. Technol.* **1976**, *49*, 1232.
(17) Valles, E. M.; Macosko, C. W. In "Chemistry and Properties of Cross-Linked Polymers"; Labana, S. S., Ed.; Academic Press: New York, 1977.
(18) Valles, E. M.; Macosko, C. W. *Macromolecules* **1979**, *12*, 673.
(19) Falender, J. R.; Yeh, G. S. Y.; Mark, J. E. *J. Chem. Phys.* **1979**, *70*, 5324.
(20) Falender, J. R.; Yeh, G. S. Y.; Mark, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 7353.
(21) Falender, J. R.; Yeh, G. S. Y.; Mark, J. E. *Macromolecules* **1979**, *12*, 1207.
(22) We are indebted to Drs. J. R. Falender and J. Saam of the Dow Corning Corp. for providing the PDMS polymer and the siloxane cross-linking agents, and information on their properties.
(23) Smith, A. L. "Analysis of Silicones"; Wiley-Interscience: New York, 1974.
(24) Mark, J. E.; Flory, P. J. *J. Appl. Phys.* **1966**, *37*, 4635.
(25) Mark, J. E. *Rubber Chem. Technol.* **1975**, *48*, 495.
(26) Flory, P. J.; Tatara, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 683.
(27) Mooney, M. *J. Appl. Phys.* **1948**, *19*, 434. Rivlin, R. S. *Philos. Trans. R. Soc. London, Ser. A* **1948**, *241*, 379.
(28) Ronca, G.; Allegra, G. *J. Chem. Phys.* **1975**, *63*, 4990.
(29) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.
(30) Flory, P. J. *Polymer* **1979**, *20*, 1317.
(31) Erman, B.; Flory, P. J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1115.
(32) Erman, B.; Flory, P. J. *J. Chem. Phys.* **1978**, *68*, 5363.
(33) K. O. Meyers and E. W. Merrill have also prepared and studied PDMS networks of high functionality (*Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **1980**, *21* (*1*), 213). Their results are difficult to interpret, however, since these experiments were apparently reproducible only to within a factor of approximately two.

Measurement of Polydispersity of Narrow Fractions and Column Spreading Parameters by Recycle Liquid Size Exclusion Chromatography

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ABSTRACT: A method has been developed, employing recycle size exclusion chromatography (GPC), to separate instrumental spreading from spreading due to the molecular weight distribution of the polymer. This is particularly important for polymers with small M_w/M_n values, such as the anionic polystyrenes, where instrumental spreading accounts for a large fraction of the total spreading. Because of interferences with the base line from impurities, a novel technique for treating the data was employed to minimize the effect of base line irregularities. The analysis separated the components of instrumental spreading into spreading due to the sample injection, σ_i, to the columns, σ_c, and to the pump and additional tubing needed for recycling, σ_p. A total of six anionic polystyrenes, including two Standard Reference Materials, SRM 705 and 1478, ranging in molecular weight from 9000 to 390 000 were analyzed in toluene and four in THF to give M_w/M_n values of 1.003–1.05. The value of σ_c increases with increasing molecular weight. In previous treatments of recycling, σ_i and σ_p were neglected, leading to less accurate values of M_w/M_n and σ_c.

The width of a peak in a liquid size exclusion chromatogram (LSEC) is due to the polydispersity of the polymer, the column spreading, and the spreading produced by injecting the polymer sample in a finite volume of solvent. For polymers with broad molecular weight distributions, the spreading due to the polydispersity of the polymer is much larger than the other components of the spreading which may therefore usually be neglected as a first approximation, and the molecular weight averages, M_w and M_n, and the polydispersity, M_w/M_n, may be computed from the chromatogram. However, for narrow fractions, the spreading due to the columns may not be neglected because it is large in relation to that due to the polydispersity of the fraction. Waters[1] and Grubisic-Gallot et al.[2] have used recycle chromatography to measure the polydispersity of narrow fractions, taking into account only the column spreading. In this treatment, we also include the spreading due to the injection as well as the additional spreading due to the pump and associated tubing required in recycle chromatography. The polydispersity, M_w/M_n, of narrow fractions may be more accurately measured by recycle chromatography than calculated from M_w and M_n