It is conceivable that the solvent residence time is slightly shorter in regions near polymer chain ends because their larger flexibility engenders faster local segmental motion. However, that this could be (if at all) the sole reason for the observed effect is conjecture. The mobility data do not indicate that, at the higher polymer concentrations, the system passes through a glass transition, but our measurements are not accurate enough to make a definite decision. We have shown, on the basis of a temperature study, that the number of polymer segments necessary to permit slippage of the (low molecular weight) chains is not exceedingly higher than that involved in solvent diffusion.

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Properties of Poly(dimethylsiloxane) Networks Prepared in Solution, and Their Use in Evaluating the Theories of Rubberlike Elasticity

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ABSTRACT: Poly(dimethylsiloxane) networks were prepared by γ irradiation of solutions of the polymer in cyclohexane; concentrations employed corresponded to volume fractions $v_{2,S}$ of polymer ranging from 0.3 to 1.0. The moduli of these networks were obtained by stress–elongation measurements on the extracted, dried networks, and the relative degrees of cross-linking were obtained by swelling equilibrium experiments. These data were used to calculate the dependence of the modulus on the volume at which the cross-linking had been carried out. Comparison of experimental and theoretical values of this quantity lends strong support to the theory of rubberlike elasticity developed by Flory and coworkers. In addition, for samples having equal moduli, deviations from the form of the theoretical stress–elongation relationship decrease with decreasing $v_{2,S}$, with the strongest such dependence apparently occurring at small values of this volume fraction. In contrast, nonequilibrium effects exhibited by these networks also decrease with decreasing $v_{2,S}$, but the largest change is observed at large values of $v_{2,S}$. At constant $v_{2,S}$, increase in degree of cross-linking seems to *increase* the cited deviations from theory but to *decrease* nonequilibrium behavior. These additional results suggest that such deviations from theory can be, at most, only partially due to nonequilibrium effects.

Although the basic features of the phenomenon of rubberlike elasticity have been well established in the molecular theories of James and Guth,[1,2] Flory and coworkers,[2,3] and Hermans,[2,4] there are still a number of unresolved issues in this area. One of the most interesting points of contention, because of its connection to the very foundations of statistical mechanics, involves the existence and magnitude of a volume-dependent contribution to the entropy and free energy of network deformation.[1–5] Since extensive discussion of the theoretical basis and magnitude of such a term has not resolved the disagreement, experiments designed to discriminate among the three theories assume particular importance. Unfortunately, however, such experiments[6] have thus far yielded results of considerable ambiguity.

Since the equations which relate the extent of swelling of a network in equilibrium with a solvent to its density of cross-links are significantly different in these theories, measurements of both the extent of equilibrium swelling and the elastic modulus of a network should permit one to establish which of the theories is most nearly correct. Of particular interest in this approach to the problem are networks prepared from polymers in solution since, in this case, the differences among the predictions of the several theories are maximized.[5] Results of such a study[5] on networks of poly(*cis*-1,4-butadiene) which had been prepared from both the bulk polymer and from its solutions in benzene were not, however, in agreement with any of the theories. In this investigation, it was concluded that the disagreement between experiment and theory was probably due to the fact that the cross-linking procedures carried out in solution involved such low polymer concentrations that there was considerable inhomogeneity in cross-linking in the resulting networks. It is quite conceivable that in such networks an estimate of cross-link density from swelling equilibrium measurements would not be appropriate, for example, in the interpretation of the elastic modulus of the same sample in uniaxial extension.[5]

It is therefore the purpose of the present study to investigate the elastic properties of networks prepared from solutions having sufficiently high polymer concentration to minimize complications due to network inhomogeneities. Poly(dimethylsiloxane) was chosen for the preparation of such networks for a variety of reasons. As shown in a previous study,[7] cross-linked samples are relatively easy to prepare, are readily extensible at room temperature, are very stable over long periods of time, and show relatively small deviations from the form of the stress–elongation relationship[1–4] predicted by the statistical theories of rubberlike elasticity. In addition,

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(1) See, for example, H. M. James and E. Guth, *J. Chem. Phys.*, **11**, 455 (1943).

(2) An extensive collection of references to the development of the molecular theory of rubberlike elasticity may be found in ref 5.

(3) See, for example, P. J. Flory, *Trans. Faraday Soc.*, **57**, 829 (1961).

(4) See, for example, J. J. Hermans, *J. Polym. Sci.*, **59**, 191 (1962).

(5) J. E. Mark, *J. Amer. Chem. Soc.*, **92**, 7252 (1970).

(6) For a recent review of earlier experimental studies as well as theoretical aspects of this problem, see K. Dušek and W. Prins, *Advan. Polym. Sci.*, **6**, 1 (1969); see also ref 5.

(7) J. E. Mark and P. J. Flory, *J. Appl. Phys.*, **37**, 4635 (1966).

the absence of double bonds in the chain backbone of poly(dimethylsiloxane) assures the absence of several of the undesirable side reactions which probably occur in the radiation cross-linking of diene polymers such as poly(*cis*-1,4-butadiene).[5] Although the main goal of this work is the testing of the molecular theories of rubberlike elasticity, the equilibrium and nonequilibrium properties of networks prepared in solution are of themselves of considerable interest.

Theory

The elastic equation of state of an unswollen polymer network in the case of uniaxial extension at the same temperature T at which the network had been prepared is given in all three theories by[5]

$$f^*/(\alpha - \alpha^{-2}) = \nu k T v_{2,\mathrm{C}}^{2/3} \tag{1}$$

where f^* is the stress per unit area of unswollen, undeformed sample and α, the elongation, is the ratio of the length of the stressed sample to the length of the unstressed, isotropic sample at the same volume.[3] The quantity ν is the number of chains per unit volume of the network, k is the Boltzmann constant, and $v_{2,\mathrm{C}}$ is the volume fraction of polymer chains in the system being cross-linked which are successfully incorporated into a network structure. (In the theory of James and Guth,[1,2] ν would be multiplied by an additional factor which could conceivably depend on the amount of diluent present during cross-linking. The fact that this complicated factor cannot be independently determined and the desire to put this theory on the same footing as the others require the assumption that this additional factor is a constant and therefore irrelevant in the case of *ratios* of moduli.) The present definition of $v_{2,\mathrm{C}}$ differs from that previously given[5] in that polymer chains which can be extracted from the network are not included in the calculation of this volume fraction. This refinement in effect treats the polymer which is not incorporated into the network as solvent, or diluent. According to eq 1, the ratio of stresses f^* or moduli $f^*/(\alpha - \alpha^{-2})$ at equal elongations of two samples which have been cross-linked in solution (S) and in the bulk (B) state, respectively, is given by

$$f_\mathrm{S}^*/f_\mathrm{B}^* = (\nu v_{2,\mathrm{C}}^{2/3})_\mathrm{S}/(\nu v_{2,\mathrm{C}}^{2/3})_\mathrm{B} \tag{2}$$

where $(v_{2,\mathrm{C}})_\mathrm{B}$ has not *a priori* been set equal to unity, for the reason already stated.

As was done previously,[5] swelling equilibrium measurements will be used to determine the ratio of cross-link densities required in eq 2 since this method provides a basis for comparing the conflicting theories. If the two networks under investigation have been prepared so as to have the same value of the volume fraction $v_{2,\mathrm{N}} \leq v_{2,\mathrm{C}}$ of polymer at swelling equilibrium in the same solvent and at the same temperature, then[5]

$$\frac{\nu_\mathrm{S}}{\nu_\mathrm{B}} = \frac{(v_{2,\mathrm{C}})_\mathrm{B}^{2/3}[1 - \omega(v_{2,\mathrm{N}}/v_{2,\mathrm{C}})_\mathrm{B}^{2/3}]}{(v_{2,\mathrm{C}})_\mathrm{S}^{2/3}[1 - \omega(v_{2,\mathrm{N}}/v_{2,\mathrm{C}})_\mathrm{S}^{2/3}]} \tag{3}$$

where ω is a constant, the magnitude of which is the point of the controversy. The theories of James and Guth,[1,2] Flory and coworkers,[2,3] and Hermans[2,4] give values of ω of 0, $^1/_2$, and 1, respectively. As was previously pointed out,[5] the theory of Hermans is inconsistent with the phenomenon of syneresis, since at the point of incipient syneresis $v_{2,\mathrm{N}} = v_{2,\mathrm{C}}$, and under these conditions the assignment $\omega = 1$ introduces the factor zero in the denominator of the right-hand side of eq 3. This theory may therefore be discounted on the basis of its inconsistency with experiment.

According to eq 2 and 3, the predicted value of the ratio of the moduli at equal elongations is given by

$$\frac{f_\mathrm{S}^*}{f_\mathrm{B}^*} = \frac{1 - \omega(v_{2,\mathrm{N}}/v_{2,\mathrm{C}})_\mathrm{B}^{2/3}}{1 - \omega(v_{2,\mathrm{N}}/v_{2,\mathrm{C}})_\mathrm{S}^{2/3}} \tag{4}$$

(This equation is a generalization of the previously obtained result[5] in which the samples prepared in solution were to have been cross-linked precisely to the syneresis point, for which $(v_{2,\mathrm{N}})_\mathrm{S} = (v_{2,\mathrm{C}})_\mathrm{S}$.) The differences between the theoretical predictions may now readily be seen from eq 4. According to the theory of James and Guth, $\omega = 0$ and $f_\mathrm{S}^*/f_\mathrm{B}^* = 1$ for samples having equal values of $v_{2,\mathrm{N}}$, irrespective of the values of $v_{2,\mathrm{C}}$ characterizing the systems from which the networks were prepared. The theory of Flory, for which $\omega = {}^1/_2$, predicts that for a pair of samples having equal $v_{2,\mathrm{N}}$ but $(v_{2,\mathrm{C}})_\mathrm{S} < (v_{2,\mathrm{C}})_\mathrm{B}$, the ratio $f_\mathrm{S}^*/f_\mathrm{B}^*$ should be significantly larger than unity.

A possible complication in obtaining experimental values of the ratio of moduli may be anticipated from the fact that observed stress–elongation relationships almost invariably depart from the simple form given in eq 1 in that $f^*/(\alpha - \alpha^{-2})$ is not independent of α.[8,9] For this reason, stress–elongation isotherms are usually expressed according to the empirical relationship[10]

$$f^*/(\alpha - \alpha^{-2}) = 2C_1 + 2C_2\alpha^{-1} \tag{5}$$

where C_1 and C_2 are unspecified constants; comparison of eq 1 and 5 shows, however, that $2C_2$ is a direct measure of the departure of the observed stress–elongation relationship from that predicted by the molecular theories. The effect of this complication is minimized by comparison of moduli at equal values of α and becomes relatively small of course for networks exhibiting small values of the constant C_2. In any case, the obscure origin of this constant makes extrapolated values of the modulus rather suspect,[9] and the required ratio of moduli is best determined at two or more values of α judged most reliable on the basis of careful consideration[5] of the errors involved in the experimental measurements.

Experimental Section

Preparation of Networks. The polymer employed was a sample of poly(dimethylsiloxane) which had a number-average molecular weight of approximately 500,000 and, to facilitate cross-linking, contained approximately 0.5 mol % $\mathrm{CH_3(CH_2{=}CH)SiO}$ units.[11] The solvent chosen for the preparation of the polymer solutions was cyclohexane; it was chosen on the basis of preliminary experiments which indicated that poly(dimethylsiloxane) in this solvent was relatively easy to cross-link using the techniques described below. The densities of the polymer and solvent at 25° were found, by pycnometry, to be 0.9700 and 0.7735 g cm^{-3}, respectively.

Weighed amounts of the degassed polymer and solvent were placed into glass tubes, which were then sealed and repeatedly inverted over a period of approximately 2 weeks in order to bring about dissolution. The volume fraction $v_{2,\mathrm{S}}$ of polymer in each solution was calculated from the densities of the components at 25°, assuming additivity of volumes. When dissolution was complete, the ends of the sample tubes were broken off. A plunger of appropriate cross section was then used to rapidly transfer each solution

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[8] Typical results may be found in the literature cited in ref 9.

[9] J. E. Mark, *J. Polym. Sci., Part C*, No. **31**, 97 (1970).

[10] M. Mooney, *J. Appl. Phys.*, **11**, 582 (1940); **19**, 434 (1948); R. S. Rivlin, *Phil. Trans. Roy. Soc. London, Ser. A*, **240**, 459, 491, 509 (1948); **241**, 379 (1948).

[11] This sample was generously provided by Dr. John Saam of the Dow-Corning Corp.

to one of a series of aluminum foil lined, aluminum molds; the wells of these molds were approximately 4 × 9 cm and were of sufficient depth to give a network which, when dried, would have a thickness of 0.1–0.2 cm. After being filled with solution, each mold was quickly sealed by means of an aluminum cover tightly held in place by a series of screws. Additional molds were filled with undiluted polymer and all samples were then cross-linked at approximately 25° by means of γ radiation from a ^{60}Co source having a radioactivity of approximately 4400 Ci. The dose rate was approximately 0.09 Mrad/hr and total doses, corrected for attenuation due to the mold itself, ranged from 0.8 to 30 Mrad. The molds were not opened for at least 6 hr after irradiation in order to permit decay of the free radicals generated in the sample. Polymer concentrations determined before and after irradiation were in good agreement, indicating that loss of solvent during the cross-linking procedure was negligible.

Extraction and Swelling Experiments. In both types of experiments, the measurements were carried out as described in detail elsewhere.[5] In brief, a portion of each cross-linked sample was placed into gently stirred benzene at room temperature, and the weight of polymer thus extracted was used to calculate values of $v_{2,C}$ from the corresponding values of $v_{2,S}$. Volume fractions $v_{2,N}$ of polymer in the networks at swelling equilibrium in cyclohexane at 25° were then determined for each of these extracted samples, again assuming additivity of volumes of solvent and polymer.

Stress–Elongation Isotherms. Samples having dimensions of approximately 0.1 × 0.6 × 6.0 cm were cut from each extracted, dried network using a precision rubber die. Stress–elongation measurements were carried out on each of these samples, at 25° and in an atmosphere of prepurified nitrogen, exactly as previously described.[5] Briefly, a cathetometer was used to measure the lengths of the demarcated test region of each sample, with the rest length L_i being measured both before and after the stress–elongation isotherm was determined. Stresses were measured in the usual manner;[5] the initial value of the stress upon elongation of the sample, its final, equilibrium value, and the time required to reach this equilibrium value were all recorded. A series of measurements at five or more elongations, consecutively increasing from $\alpha \cong 1.1$ to 1.8, was carried out for each network except for the case of several prepared at the lowest polymer concentration ($v_{2,S} = 0.30$); these networks ruptured before the maximum elongation $\alpha = 1.8$ could be attained.

Results and Discussion

Eight networks prepared by cross-linking samples in the bulk, undiluted state ($v_{2,S} = 1.0$) were labeled B-1–B-8, and are described in the uppermost portion of Table I. Additional networks were prepared from each of six solutions, S1–S6, having volume fractions $v_{2,S}$ of polymer of 0.75, 0.62, 0.55, 0.48, 0.40, and 0.30, respectively; these networks are described in the remaining part of the table. The radiation doses used to cross-link the samples are given in the third column of the table; the increase in dose with decrease in $v_{2,S}$ was employed in order that all series of samples corresponding to a value of $v_{2,S}$ have approximately the same range of $v_{2,N}$. (As pointed out previously,[5] the efficiency of intermolecular cross-linking in systems containing significant amounts of diluent is relatively low and also, a considerably larger number of cross-links must be introduced in such cases to give a network having the same equilibrium degree of swelling as one prepared in the absence of diluent.) The fourth column presents values of $v_{2,C}$ which were obtained from the corresponding values of $v_{2,S}$ by correction for the amount of polymer not incorporated into the network. For convenience in interpretation, each network of a series prepared at a fixed value of $v_{2,S}$ was assumed to have the average value of $v_{2,C}$ of that series; for the series B, S1–S6, these values are 0.910 (±0.014), 0.691 (±0.011), 0.579 (±0.005), 0.515 (±0.010), 0.454 (±0.011), 0.379 (±0.002), and 0.281 (±0.001). Column five of the table records values of $v_{2,N}$, the volume fraction of polymer at swelling equilibrium, for each network in cyclohexane at 25°.

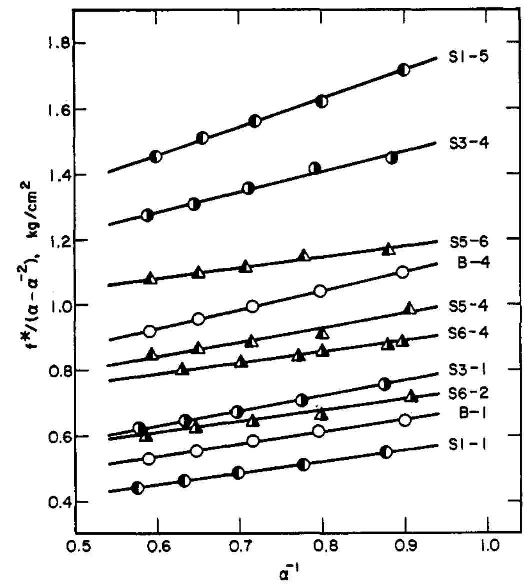

Figure 1. The modulus $f^*/(\alpha - \alpha^{-2})$ shown as a function of the reciprocal elongation for selected samples of poly(dimethylsiloxane) networks in the unswollen state, at 25°. See text and Table I for details.

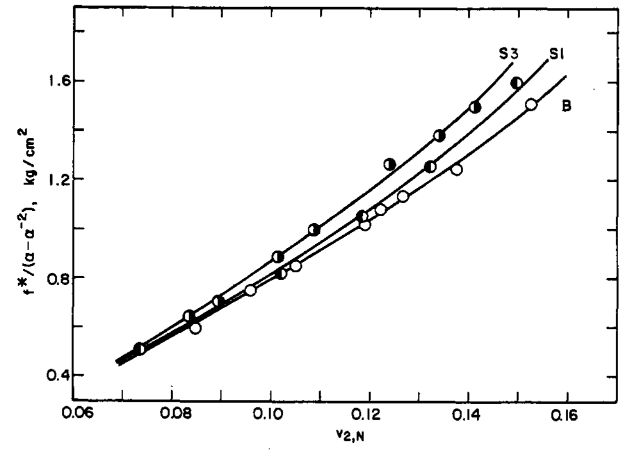

Figure 2. The relationship between the modulus at $\alpha = 1.300$ and the volume fraction of polymer present at swelling equilibrium, in cyclohexane at 25°, for networks prepared from bulk polymer (○) and from polymer solutions S1 (◐) and S3 (◑).

The modulus $f^*/(\alpha - \alpha^{-2})$ was plotted against the reciprocal elongation, as suggested by eq 5, and the least-squares method was used to locate the best straight line representing each stress–elongation isotherm. Typical results are shown in Figure 1. Values of $f^*/(\alpha - \alpha^{-2})$ at $\alpha = 1.300$ are recorded for all samples in column six of the table, and the slope of each line, $2C_2$ in eq 5, is given in the following column. These values of the modulus were plotted against $v_{2,N}$ for each series B, S1–S6. Results for B, S1, and S3 are shown in Figure 2; for reasons of clarity, the results for S2, S4–S6 have not been included. Interpolation of these results was used to obtain experimental values of the ratio f_S^*/f_B^* at each average value of $(v_{2,C})_S$, at values of $v_{2,N}$ of 0.09 and 0.12. (As can be seen from Table I, choice of larger values of $v_{2,N}$ would exclude results on several series of networks prepared at the lower values of $v_{2,S}$.) These values of the ratio, and values obtained

TABLE I
SAMPLE CHARACTERISTICS AND STRESS–ELONGATION RESULTS

Sample	$v_{2,S}$	Radiation dose, Mrads	$v_{2,C}$	$v_{2,N}$	$f^*/(\alpha - \alpha^2)$,[a] kg/cm²	$2C_2$, kg/cm²	Av time required for equil, hr	$\left[\frac{f^*\text{ (equil)}}{f^*\text{ (init)}}\right]_{av}$
B-1	1.00	0.85	0.879	0.0848	0.600	0.375	1.25	0.855
B-2	1.00	1.06	0.893	0.0959	0.752	0.530	1.20	0.888
B-3	1.00	1.19	0.901	0.105	0.853	0.634	1.17	0.919
B-4	1.00	1.32	0.914	0.119	1.02	0.575	0.83	0.935
B-5	1.00	1.46	0.914	0.122	1.08	0.630	0.70	0.948
B-6	1.00	1.55	0.920	0.127	1.14	0.773	0.70	0.959
B-7	1.00	1.69	0.927	0.138	1.25	0.605	0.73	0.958
B-8	1.00	2.08	0.934	0.152	1.51	0.850	0.43	0.979
S1-1	0.75	1.02	0.669	0.0734	0.510	0.355	1.26	0.857
S1-2	0.75	1.48	0.684	0.102	0.821	0.490	0.85	0.945
S1-3	0.75	2.03	0.702	0.119	1.05	0.580	0.48	0.975
S1-4	0.75	2.46	0.698	0.132	1.26	0.720	0.28	0.987
S1-5	0.75	3.48	0.701	0.150	1.60	0.845	0.15	0.993
S2-1	0.62	1.11	0.565	0.0844	0.660	0.496	0.70	0.923
S2-2	0.62	1.73	0.577	0.105	0.917	0.614	0.28	0.972
S2-3	0.62	2.27	0.581	0.118	1.06	0.595	0.10	0.988
S2-4	0.62	3.31	0.586	0.133	1.37	0.721	0.15	0.994
S2-5	0.62	4.07	0.583	0.138	1.45	0.752	0.07	0.996
S2-6	0.62	5.17	0.583	0.145	1.58	0.839	0.03	0.998
S3-1	0.55	1.44	0.496	0.0837	0.636	0.435	0.53	0.943
S3-2	0.55	1.60	0.547	0.0896	0.704	0.445	0.58	0.950
S3-3	0.55	2.43	0.507	0.102	0.888	0.515	0.22	0.979
S3-4	0.55	2.60	0.508	0.109	1.01	0.627	0.30	0.989
S3-5	0.55	4.08	0.514	0.124	1.27	0.690	0.08	0.995
S3-6	0.55	5.90	0.515	0.134	1.39	0.620	0.02	0.999
S3-7	0.55	8.04	0.516	0.141	1.50	0.635	0.00	0.999
S4-1	0.48	2.87	0.465	0.105	0.904	0.442	0.08	0.990
S4-2	0.48	4.08	0.439	0.111	1.04	0.680	0.02	0.996
S4-3	0.48	6.02	0.441	0.119	1.14	0.614	0.01	0.998
S4-4	0.48	7.60	0.449	0.123	1.20	0.577	0.01	0.997
S4-5	0.48	9.76	0.449	0.127	1.22	0.449	0.01	0.997
S4-6	0.48	11.7	0.469	0.135	1.35	0.534	0.00	0.998
S4-7	0.48	13.7	0.469	0.138	1.41	0.419	0.00	0.995
S5-1	0.40	2.89	0.377	0.0866	0.668	0.390	0.08	0.980
S5-2	0.40	4.12	0.377	0.0947	0.766	0.400	0.07	0.991
S5-3	0.40	6.54	0.382	0.103	0.861	0.400	0.03	0.995
S5-4	0.40	9.67	0.378	0.107	0.903	0.345	0.00	0.998
S5-5	0.40	12.8	0.380	0.113	0.968	0.345	0.00	0.999
S5-6	0.40	16.9	0.381	0.124	1.14	0.320	0.00	0.999
S6-1	0.30	7.52	0.281	0.0816	0.612	0.200	0.05	0.984
S6-2	0.30	10.6	0.280	0.0864	0.663	0.345	0.02	0.994
S6-3	0.30	14.6	0.280	0.0916	0.705	0.335	0.02	0.996
S6-4	0.30	20.8	0.280	0.103	0.843	0.320	0.00	0.999
S6-5	0.30	25.6	0.285	0.118	0.966	0.140	0.00	0.999
S6-6	0.30	29.8	0.282	0.122	1.12	0.125	0.00	1.000

[a] Elongation of $\alpha = 1.300$.

in the same manner at $\alpha = 1.700$, are presented in Table II. All of the values exceed unity as predicted by the theory of Flory,[3] and the magnitude of the ratio is in good agreement with values predicted from that theory. (Calculations using the less appropriate volume fraction $v_{2,S}$ in place of $v_{2,C}$ gave values of f_S^*/f_B^* from the Flory theory that differed from those listed in the last column by less than 1%.) Because of possible complications due to unusual network topologies in the case of networks prepared at very low polymer concentrations,[5] the results in Table II corresponding to $(v_{2,C})_S \geq 0.45$ are probably the most reliable. These results confirm the prediction of the Flory theory that the ratio f_S^*/f_B^* should increase with decreasing $(v_{2,C})_S$, and they seem to give preliminary confirmation of the additional prediction of this theory that the ratio should increase with increasing $v_{2,N}$. The fact that the values of the ratio obtained at two rather different values of α do not differ greatly indicates that complications due to nonzero values of $2C_2$ are relatively minor.

Some additional properties of these networks which are of interest are given in the last three columns of Table I. The decrease in $2C_2$ with decreasing $v_{2,S}$ or $v_{2,C}$ at constant values of the modulus is in agreement with the previous, more limited results obtained on networks prepared from poly(*cis*-1,4-butadiene),[5,9] and from natural rubber.[12] The values of $2C_2$ reported in Table I are probably most reliable in the region of $f^*/(\alpha - \alpha^{-2}) \geq 1.0$ kg/cm^2; these results seem to suggest that the dependence of $2C_2$ on $v_{2,\mathrm{S}}$ is strongest in the region $v_{2,\mathrm{S}} < 0.5$. In contrast, the time required to reach mechanical equilibrium, while also decreasing with decreasing $v_{2,\mathrm{S}}$ at constant values of the modulus, changes most markedly in the region of *large* $v_{2,\mathrm{S}}$; a similar dependence is shown by the amount of stress relaxation occurring in a sample, as measured by the ratio of the equilibrium value of the stress to the initial value observed immediately upon sample elongation. Very importantly, at constant $v_{2,\mathrm{S}}$, increase in degree of cross-linking seems in general to *increase* $2C_2$ but to *decrease* the nonequilibrium effects. These differences in behavior between $2C_2$ and the nonequilibrium characteristics would seem to support the previously reached conclusion[7] that, at least in the case of poly(dimethylsiloxane) networks, the $2C_2$ correction is not entirely due to nonequilibrium effects. Values of the sample rest lengths L_i obtained before and after the stress–elongation measurements were identical within experimental error and therefore such results, which have been used to characterize the permanent deformation of a sample,[5,9] are not included here. A final point of interest is the fact that only the networks prepared at the lowest polymer concentration ($v_{2,\mathrm{S}} = 0.30$) ruptured in the elongation range $\alpha = 1.1$–1.8, even though their moduli were very similar in magnitude to those of samples prepared at other, larger values of $v_{2,\mathrm{S}}$. These additional results seem to support earlier contentions[5,9,12] that networks prepared by cross-linking a polymer in solution have very different topologies from those prepared in the bulk, undiluted state.

TABLE II
VALUES OF $f_\mathrm{S}^*/f_\mathrm{B}^*$

		Experimental		Theoretical	
$(v_{2,\mathrm{C}})_\mathrm{S}$	$v_{2,\mathrm{N}}$	$\alpha = 1.3$	$\alpha = 1.7$	James, Guth	Flory
0.69	0.09	1.04	1.03	1.00	1.02
	0.12	1.05	1.03	1.00	1.03
0.58	0.09	1.07	1.06	1.00	1.04
	0.12	1.09	1.08	1.00	1.05
0.52	0.09	1.08	1.07	1.00	1.06
	0.12	1.12	1.13	1.00	1.07
0.45	0.09	1.09	1.08	1.00	1.08
	0.12	1.10	1.12	1.00	1.09
0.38	0.09	1.04	1.07	1.00	1.10
	0.12	1.05	1.09	1.00	1.13
0.28	0.09	1.03	1.07	1.00	1.17
	0.12	1.01	1.08	1.00	1.21

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Vapor Sorption of *N,N*-Dimethylformamide on Poly(γ-benzyl α,L-glutamate)[1]

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ABSTRACT: Solvent activities for poly(γ-benzyl L-glutamate) solutions in *N,N'*-dimethylformamide have been determined at 25, 20, and 10° in the concentration range 70–100 vol % polymer. The results indicate that solvent activity is insensitive to temperature at constant composition in the concentration and temperature ranges studied. No evidence was found for the coexistence of two phases or for ordered side chains in the polypeptide. The results are compared with theories of solutions of rodlike molecules.

It is known that poly(γ-benzyl L-glutamate) (PBLG) dissolves in *N,N'*-dimethylformamide (DMF) in the form of the rodlike, α-helical conformation.[2] Only limited thermodynamic studies have been made on this system. At low polymer concentration the solutions are isotropic, while at higher concentrations they are anisotropic (liquid crystalline). Coexistence of isotropic and anisotropic phases is observed in an intermediate concentration range.[3] The temperature–composition phase diagram in the range −20 to 140° and 0–30 vol % polymer has been determined recently.[3] Solvent activities of dilute, isotropic solutions measured as a function of temperature and of solute molecular weight have been reported also.[4] In this paper we report the results of solvent activity measurements at 25, 20, and 10° and in the composition range 70–100 vol % polymer. The results are compared with the existing theories and with similar experimental work of Flory and Leonard.[5]

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