Evaluation of the Theories of Rubber-like Elasticity Using Swollen Networks Cross-Linked at Different Degrees of Dilution

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ABSTRACT: A recently reported study described the preparation of elastomeric networks by cross-linking poly(dimethylsiloxane) chains in both the undiluted state and in solution. Measurements of the moduli of these networks in the *unswollen* state gave results supporting the theory of rubber-like elasticity developed by Flory and coworkers, rather than the corresponding theory due to James and Guth. These results were not entirely unambiguous, however, because of complications due to departures ("$2C_2$ corrections") from the expected elastic equation of state. Much of this uncertainty has now been removed by measurements of the moduli of such networks in the *swollen* state, a condition under which the effects of the $2C_2$ contributions are known to be minimized. These new results strongly support the earlier conclusion that the Flory theory is the more nearly correct. Nonequilibrium effects, as well as the $2C_2$ corrections, diminish upon incorporation of a diluent into the cross-linked network; similar decreases occur if diluent had been present during the cross-linking process, even if such diluent is removed prior to the stress-strain measurements. Analysis of these additional results suggests that the $2C_2$ correction cannot be entirely due to nonequilibrium effects.

An important controversy in the area of rubber-like elasticity centers on the existence and magnitude of a volume-dependent contribution to the entropy change accompanying network deformation.[1-5] The two conflicting molecular theories in this area are those of James and Guth[6] and Flory.[7] (A third theory[8] fails to survive the requirement that it be consistent with the existence of syneresis in swollen polymer networks.[3,4]) In these two theories, 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; measurements of both the extent of equilibrium swelling and the elastic modulus of a network could therefore be used to establish which of the theories is more nearly correct.[3,4] Of particular interest in this approach to the problem are networks prepared by cross-linking polymers *in solution* since, under these conditions, the differences between the predictions of the two theories can be made sufficiently large to permit discrimination between them on experimental grounds.[2-5]

In essence, the experimental method employed involves the determination of the ratio of the moduli of two polymer networks which have the same equilibrium extent of swelling (in the same solvent at the same temperature) but which differ markedly in the volume at which the cross-links of the network had been introduced. Such a study[4] on elongated networks of poly(dimethylsiloxane) (PDMS) gave results which in general strongly supported the theory developed by Flory.[7] The results were somewhat ambiguous, however, in the case of networks prepared at relatively low polymer concentration, a particularly unfortunate circumstance since it is in this region that the differences between the predictions of the two theories are most pronounced.[3,4] Detailed analysis of these results now indicates that this ambiguity is almost certainly due to deviations of the observed stress-strain relationships from that predicted by theory.[6-8] Such deviations are almost always observed in stress-elongation measurements.[9,10] Although relatively small in the present instance, they are apparently not negligible in their effect and, furthermore, appear to vary in magnitude with the polymer concentration in the system which had been used to form the network. Fortunately, it is now well established that such deviations are minimized in the case of networks which are swollen with diluent prior to the stress-strain measurements. Reinvestigation of the various samples of interest, now in the swollen state, would therefore offer the possibility of simultaneously diminishing the magnitude of such deviations in general and suppressing their apparent dependence on the concentration of polymer in the system being used to prepare the cross-linked samples.

The purpose of the present study is therefore to determine the moduli of the samples previously investigated in the unswollen state, and several other similar samples as well, now using a sufficiently high degree of network swelling to make less ambiguous the desired evaluation of the contending theories. Although the main goal of this work is this testing of the molecular theories of rubber-like elasticity, the equilibrium and nonequilibrium properties of networks prepared in solution and studied in the swollen state are of themselves of considerable interest.

Theory

The equation of state of a uniaxially extended polymer network swollen to a volume fraction of polymer v_2 is given in both theories by the equations

$$f^*/(\alpha - \alpha^{-2}) = (\nu kT/L_i A^*)(V/V_0)^{2/3}$$

$$f^* {v_2}^{1/3}/(\alpha - \alpha^{-2}) = (\nu kT/V^*)(V^*/V_0)^{2/3} \qquad (1)$$

where f^* is the stress divided by the area A^* of the unswollen undeformed sample of volume V^*, ν is the number of chains in the network, k is the Boltzmann constant, and T is the absolute temperature. The volume V is that of the network in the elongated state, V_0 is the volume such that the mean-square end-to-end distance of the network chains is that of the free, unperturbed chains, and α, the elongation, is the ratio of the length of the stressed sample to the length L_i of the unstressed, isotropic swollen sample at the same volume V.[7] Since, in elasticity theory, the network "chains" consist of those parts of the original polymer chain now lying between two consecutive cross-

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(1) Recent discussions of this controversy may be found in ref 2-5. An extensive collection of references to the development of the molecular theory of rubber-like elasticity in general may be found in ref 2 and 3.

(2) K. Dušek and W. Prins, *Advan. Polym. Sci.*, **6**, 1 (1969).

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

(4) R. M. Johnson and J. E. Mark, *Macromolecules*, **5**, 41 (1972).

(5) D. Froelich, D. Crawford, T. Rozek, and W. Prins, *Macromolecules*, **5**, 100 (1972).

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

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

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

(9) Typical results may be found in the literature cited in ref 10.

(10) J. E. Mark, *J. Polym. Sci., Part C*, **31**, 97 (1970).

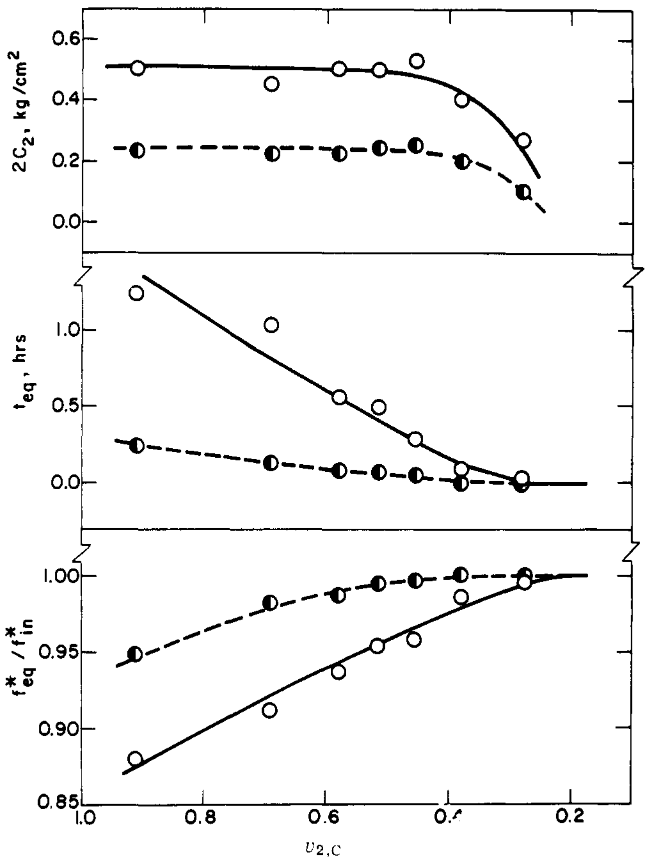

Figure 1. The effect of $v_{2,C}$ (the volume fraction of PDMS chains in the system being cross-linked which are successfully incorporated into a network structure) on the following properties of the resulting networks: the $2C_2$ correction, the average length of time t_{eq} required to reach mechanical equilibrium, and the average value of the ratio f_{eq}^*/f_{in}^* of the equilibrium value of the force to the initial value exhibited immediately upon elongation. These illustrative results pertain to networks having a volume fraction of polymer at swelling equilibrium in cyclohexane of $v_{2,N} = 0.09$. Open circles and solid lines locate results obtained on networks in the unswollen state; the half-filled circles and dotted lines locate results for the same networks when swollen with dimethylsiloxane oligomer to a volume fraction of polymer of $v_2 = 0.600$. All results pertain to 25°.

links, such network chains are relatively short and should therefore be in their unperturbed state to good approximation, even when formed in the presence of thermodynamically good solvents. In addition, if eq 1 is applied at the same temperature at which the polymer was cross-linked, as will be the case, then V_0 may be identified with the volume at which the network was prepared. Use of eq 1 in conjunction with cross-link densities determined from swelling equilibrium measurements then yields the following equation for the ratio of stresses f^* or moduli $f^*/(\alpha - \alpha^{-2})$ at equal elongations of two swollen networks which have been cross-linked in solution (S) and in the bulk (B) state, respectively, but which have the same value of the volume fraction $v_{2,N}$ of polymer at swelling equilibrium in the same solvent and at the same temperature

$$\frac{f_S^*}{f_B^*} = \frac{1 - \omega(v_{2,N}/v_{2,C})_B^{2/3}}{1 - \omega(v_{2,N}/v_{2,C})_S^{2/3}} \tag{2}$$

In this equation, which is identical with that obtained for the comparison of unswollen networks,[4] $v_{2,C}$ is the volume fraction of polymer chains in the system being cross-linked which are successfully incorporated into a network structure, upon cross-linking polymer in a solution in which its volume fraction is $v_{2,S}$. The quantity ω is the coefficient on which the controversy centers. According to the theory of James and Guth, $\omega = 0$ and $f_S^*/f_B^* = 1$ for samples having equal values of $v_{2,N}$, irrespective of the values of $v_{2,C}$ characterizing the systems from which the networks were prepared. The theory of Flory, for which $\omega = \frac{1}{2}$, predicts that for a pair of samples having equal $v_{2,N}$ but $(v_{2,C})_S < (v_{2,C})_B$, the ratio f_S^*/f_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, already mentioned, that observed stress-elongation relationships almost invariably depart from the simple form given in equation 1 in that $f^*v_2^{1/3}/(\alpha - \alpha^{-2})$ is not independent of α.[9,10] For this reason, stress-elongation isotherms are usually expressed according to the empirical relationship[11]

$$f^*v_2^{1/3}/(\alpha - \alpha^{-2}) = 2C_1 + 2C_2\alpha^{-1} \tag{3}$$

where $2C_1$ and $2C_2$ are unspecified constants; comparison of eq 1 and 3 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 $2C_2$ correction.

Experimental Section

The networks used in this study were, with few exceptions, the same networks investigated previously in the unswollen state.[4] Since several samples were no longer suitable for additional measurements, a few more networks were prepared; for these, the conditions of preparation, extraction of soluble constituents, and determination of the volume fraction of polymer $v_{2,N}$ at swelling equilibrium in cyclohexane at 25° were precisely those used for the other samples.[4] The diluent chosen to swell all of the polymer networks was a nitrogen-purged liquid dimethylsiloxane oligomer[12] having a molecular weight of approximately 10^4 and a density at 25° of 0.966 g/cm^3. The fact that this diluent is virtually identical with the network chains prevents complications from specific solvent interactions known to affect PDMS chains both in solution[13] and in swollen networks.[14] Preliminary experiments indicated that the maximum degree of swelling feasible for all of the networks in this diluent at 25° corresponded to a volume fraction of polymer v_2 of approximately 0.6. Each network was therefore swollen with dimethylsiloxane oligomer to an extent corresponding to 0.600 (±0.001) on the assumption of perfect additivity of volumes. After sufficient time (48 hr) had elapsed to assure swelling uniformity, stress-strain isotherms were determined for these swollen networks at this constant composition and at 25°, in exactly the manner described in the earlier studies.[3,4] As was previously the case,[3,4] highly reproducible isotherms were obtained by these procedures.

Results and Discussion

The seven networks prepared by cross-linking samples in the bulk, undiluted state ($v_{2,S} = 1.0$) were labeled B-1 through B-7 and are described in the uppermost portion of Table I. The networks 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, were given analogous designations and 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 and values of $v_{2,S}$ which were obtained from the corresponding

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

(12) This diluent was generously provided by the Silicones Division of the Union Carbide Corp.; the sample designation was Y-4978.

(13) V. Crescenzi and P. J. Flory, *J. Amer. Chem. Soc.*, **86**, 141 (1964).

(14) C. U. Yu and J. E. Mark, *Macromolecules*, in press.

Table I
Characteristics of the PDMS Networks and Their Stress-Elongation Properties in the Swollen State[a]

Sample	$v_{2,S}$	Radiation Dose (Mrads)	$v_{2,C}$	$v_{2,N}$	$f^*v_2^{1/3}/(\alpha - \alpha^{-2})$[b] (kg/cm²)	$2C_2$ (kg/cm²)	Av Time Reqd for Equil (hr)	$\left[\frac{f^*\text{ (equil)}}{f^*\text{ (init)}}\right]_{av}$
B-1	1.00	0.85	0.879	0.0848	0.432	0.195	0.21	0.944
2	1.00	1.06	0.893	0.0959	0.595	0.278	0.26	0.956
3	1.00	1.19	0.901	0.105	0.666	0.287	0.24	0.967
4	1.00	1.32	0.914	0.119	0.838	0.315	0.09	0.987
5	1.00	1.46	0.914	0.122	0.895	0.323	0.19	0.989
6	1.00	1.55	0.920	0.127	0.905	0.357	0.18	0.986
7	1.00	1.69	0.927	0.138	1.01	0.348	0.10	0.990
S1-1	0.75	1.02	0.669	0.0734	0.363	0.146	0.18	0.957
2	0.75	1.48	0.684	0.102	0.671	0.285	0.09	0.994
3	0.75	2.03	0.702	0.119	0.873	0.281	0.05	0.998
4	0.75	2.46	0.698	0.132	1.11	0.376	0.00	1.000
5	0.75	3.48	0.701	0.150	1.39	0.449	0.00	1.000
S2-1	0.62	1.11	0.565	0.0844	0.494	0.177	0.31	0.971
2	0.62	1.73	0.577	0.105	0.752	0.294	0.00	1.000
3	0.62	2.27	0.581	0.118	0.899	0.305	0.00	1.000
4	0.62	3.31	0.586	0.133	1.15	0.316	0.00	1.000
5	0.62	4.07	0.583	0.138	1.25	0.370	0.00	1.000
6	0.62	5.17	0.583	0.145	1.35	0.407	0.09	0.992
S3-1	0.55	1.44	0.496	0.0837	0.486	0.160	0.09	0.992
2	0.55	1.60	0.547	0.0896	0.572	0.240	0.07	0.994
3	0.55	2.43	0.507	0.102	0.747	0.310	0.00	1.000
4	0.55	2.60	0.508	0.109	0.838	0.296	0.07	0.999
5	0.55	4.08	0.514	0.124	1.07	0.215	0.00	1.000
6	0.55	5.90	0.515	0.134	1.23	0.217	0.00	1.000
S4-1	0.48	1.65	0.402	0.0446	0.478	0.190	0.22	0.970
2	0.48	2.12	0.443	0.0896	0.567	0.221	0.06	0.990
3	0.48	2.87	0.465	0.105	0.776	0.275	0.06	0.999
4	0.48	4.08	0.439	0.111	0.863	0.275	0.00	1.000
5	0.48	6.02	0.441	0.119	0.990	0.236	0.00	1.000
6	0.48	7.60	0.449	0.123	1.04	0.268	0.00	1.000
7	0.48	13.70	0.469	0.138	1.26	0.215	0.05	0.999
S5-1	0.40	2.89	0.377	0.0866	0.554	0.167	0.00	1.000
2	0.40	4.12	0.377	0.0947	0.666	0.235	0.00	1.000
3	0.40	6.54	0.382	0.103	0.769	0.242	0.00	1.000
4	0.40	9.67	0.378	0.107	0.790	0.127	0.00	1.000
5	0.40	12.8	0.380	0.113	0.912	0.079	0.00	1.000
6	0.40	16.9	0.381	0.124	1.01	0.111	0.00	1.000
S6-1	0.30	3.48	0.268	0.0692	0.402	0.119	0.08	0.997
2	0.30	5.49	0.281	0.0762	0.461	0.122	0.04	0.999
3	0.30	7.52	0.281	0.0816	0.519	0.083	0.00	1.000
4	0.30	10.6	0.280	0.0864	0.545	0.102	0.00	1.000
5	0.30	14.6	0.280	0.0916	0.602	0.076	0.00	1.000
6	0.30	20.8	0.280	0.103	0.719	0.043	0.00	1.000
7	0.30	30.1	0.279	0.124	0.848	0.045	0.00	1.000
8	0.30	36.7	0.279	0.127	0.904	0.026	0.00	1.000

[a] Swollen in dimethylsiloxane fluid at 25° to a volume fraction of polymer of $v_2 = 0.600$. [b] Elongation of $\alpha = 1.300$.

values of $v_{2,C}$ by correction for the amount of polymer not incorporated into the network are given in the following column. 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 0.907 (±0.014), 0.691 (±0.011), 0.579 (±0.005), 0.515 (±0.011), 0.454 (±0.011), 0.379 (±0.002), and 0.279 (±0.002), respectively. 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°.

The modulus $f^*v_2^{1/3}/(\alpha - \alpha^{-2})$ was plotted against the reciprocal elongation, as suggested by eq 3, and the least-squares method was used to locate the best straight line representing each stress–elongation isotherm. Values of $f^*v_2^{1/3}/(\alpha - \alpha^{-2})$ at $\alpha = 1.300$ are recorded in column six of the table, and the slope of each line, $2C_2$ in eq 3, is given in the following column. The remaining two columns record quantities which can serve as measures of the amount of noninstantaneous chain motion occurring as a result of the imposed stress. The first of these quantities is the average amount of time t_{eq} required to reach mechanical equilibrium in the elongated network, and the second is the average value of the ratio f_{eq}^*/f_{in}^* of the force at equilibrium to its initial value, immediately upon elongation.

We discuss first the values of $2C_2$ and their possible correlation with the two nonequilibrium properties t_{eq} and f_{eq}^*/f_{in}^*. Figure 1 shows plots of these three quantities as a function of $v_{2,C}$ at $v_{2,N} = 0.09$, an illustrative value of $v_{2,N}$ to be used in the comparison of the moduli as well. Open circles in this and the following figure locate results obtained from the previous study[4] of the unswollen networks, and half-filled circles to results obtained from

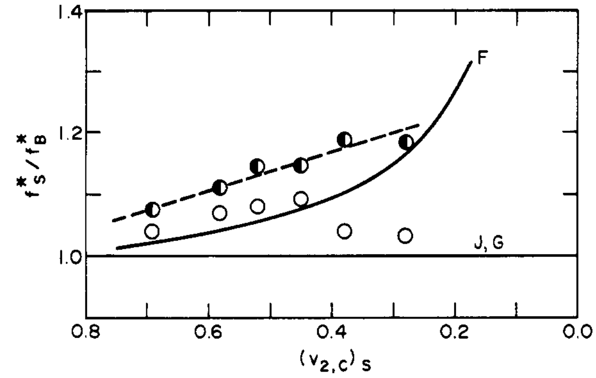

Figure 2. The ratio of the modulus f_S^* of a PDMS network prepared in solution to the modulus f_B^* of a PDMS network having the same value of $v_{2,N}$ (0.09) but prepared in the bulk (undiluted) state, shown as a function of $v_{2,C}$ characterizing the networks prepared in solution (see text and legend to Figure 1). The experimental results were obtained at an elongation α of 1.300; open circles pertain to results obtained on the unswollen networks, and half-filled circles and the dotted line pertain to results obtained for the swollen networks. The two solid lines represent the theoretical results predicted by James and Guth[6] and by Flory.[7] Additional results are given in Table II.

the present study on the swollen networks. It is immediately seen that both cross-linking in solution ($v_{2,C} < 1$) and incorporation of a diluent into a polymer network ($v_2 < 1$) have the same general effect: a decrease in both the correction $2C_2$ and the nonequilibrium behavior (decrease in t_{eq} and increase in f_{eq}^*/f_{in}^*). Whereas t_{eq} and f_{eq}^*/f_{in}^* change most rapidly in the region of relatively large $v_{2,C}$, however, the quantity $2C_2$ is approximately constant in this range, decreasing only for values of $v_{2,C}$ less than approximately 0.5. As pointed out previously,[4] these results and others as well[2,4,15] suggest that the $2C_2$ correction cannot be entirely due to nonequilibrium effects.

With regard to the determination of experimental values of the ratio f_s^*/f_B^*, it is important to note from the uppermost portion of Figure 1 that $2C_2$ changes most rapidly with $v_{2,C}$ for $v_{2,C} < 0.5$, the range where the values of f_S^*/f_B^* for the unswollen networks did not definitively support either of the two theories of rubber-like elasticity.[4] It is also obvious from this portion of Figure 1 that incorporation of diluent into these networks does have the desired effect of both significantly diminishing the values of $2C_2$ in general and decreasing their dependence on $v_{2,C}$. The desired ratio of stresses or moduli was now obtained by plotting values of $f^* v_2^{1/3}/(\alpha - \alpha^{-2})$ at selected values of α *vs.* $v_{2,N}$ for each series B, S1–S6. Interpolation and, in one case, a limited extrapolation were then used to obtain experimental values of f_S^*/f_B^* at values of α *and* $v_{2,N}$ judged to be most reliable on experimental grounds: α = 1.300 and 1.700 and $v_{2,N}$ = 0.09 and 0.12. Figure 2 shows these results, along with the previous results[4] obtained for the unswollen networks as a function of the average value of $v_{2,C}$ for the solution cross-linked samples, for the illustrative case $v_{2,N}$ = 0.09 and α = 1.300. The two solid lines in this figure show the results predicted by the theories of James and Guth[6] and Flory.[7] The present experimental results strongly support the theory of Flory, rather than that of James and Guth in that f_S^*/f_B^* is invariably larger than unity, to an extent well beyond the experimental uncertainty in such measurements, is of approximately the magnitude predicted by the theory of Flory, and unquestionably increases monotonically as $v_{2,C}$ characterizing the solution cross-linked sample decreases. These experimental and theoretical results, and others corresponding to other values of $v_{2,N}$ and α, are summarized in Table II. The entire collection of results gives exceedingly strong support to the conclusion, previously reached on the basis of less definitive data,[4] that the theory of rubber-like elasticity developed by Flory[7] is the more nearly correct.[16]

Table II
Values of f_S^*/f_B^* for Swollen PDMS Networks

		Experimental		Theoretical	
$(v_{2,C})_S$	$v_{2,N}$	α = 1.3	α = 1.7	James and Guth	Flory
0.69	0.09	1.07	1.06	1.00	1.02
	0.12	1.04	1.06	1.00	1.03
0.58	0.09	1.11	1.11	1.00	1.04
	0.12	1.09	1.10	1.00	1.05
0.52	0.09	1.14	1.14	1.00	1.06
	0.12	1.17	1.19	1.00	1.07
0.45	0.09	1.16	1.16	1.00	1.08
	0.12	1.16	1.20	1.00	1.09
0.38	0.09	1.19	1.21	1.00	1.10
	0.12	1.13	1.19	1.00	1.13
0.28	0.09	1.18	1.21	1.00	1.17
	0.12	1.08	1.15	1.00	1.21

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(15) See, for example, J. E. Mark and P. J. Flory [*J. Appl. Phys.*, 37, 4635 (1966)] and references cited therein.

(16) Prins and coworkers also reach the conclusion that the Flory theory is the more nearly correct on the basis of the modulus, equilibrium swelling, and swelling pressure of polystyrene networks swollen with benzene; see ref 5.