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An Experimental Comparison of the Theories of Elasticity of Polymer Networks

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Abstract: The three main theories of rubberlike elasticity yield expressions for the elastic free energy of a network made up of Gaussian chains which differ significantly with respect to a volume-dependent contribution to the entropy. In the present study, the validity of each of these theoretical expressions is gauged by measuring the ratio of the moduli of two networks of *cis*-1,4-polybutadiene which have the same equilibrium extent of swelling but differ markedly in the volume at which the chemical cross-links had been introduced: one series of samples had been cross-linked in the bulk (undiluted) state, another in dilute solution to the syneresis point. The relationship derived by Hermans is shown to be inconsistent with the existence of syneresis and thus is clearly unacceptable. Neither the theory of James and Guth nor that of Flory and coworkers succeeds in predicting the magnitude of the ratio of the moduli or its dependence on the degree of cross-linking. Of the networks studied, those formed in solution showed significantly smaller departures from the predicted form of the dependence of stress on strain and considerably smaller nonequilibrium, relaxation effects. These differences are used to provide a qualitative interpretation of the discrepancies between theory and experiment in terms of network topology.

The foundations of the statistical-mechanical theory of the elasticity of polymer networks have been laid by three main groups of workers, namely by James and Guth,[1-6] by Wall and Flory and coworkers,[7-14] and by Hermans.[15,16] In independent, theoretical investigations these groups have obtained expressions for the crucially important entropy of network deformation which differ with respect to the existence and magnitude of a volume-dependent contribution. Extensive discussions[5,6,11,15,16] of this point of contention have not brought about agreement, and the controversy has continued to the present time.

Experimental evidence bearing on this problem is sparse, because the contested entropic contribution does not affect the predicted elastic equation of state, the fundamental equation of rubber elasticity which relates a network's retractive force to its extent of deformation, temperature, and structure. The equations, however, which relate the extent of swelling of a network in contact with an excess of solvent to its density of cross-links are markedly different in the three theories. This predicted difference has served as a basis for several attempts[17-19] to determine which of the present theories is most nearly correct. The results have been ambiguous and have not definitely supported any one theory. Furthermore, the independent measure of the effective cross-link density of the network which is required for the interpretation of some of the measurements was obtained by assuming the chemical cross-linking agent reacted stoichiometrically with the polymer to form a highly idealized structure. This is an exceedingly poor assumption for a number of reasons, including the possible loss of reagent in side reactions and the formation of network defects which are ineffective in the elastic response of the network.[20,21]

It is the purpose of the present study to attempt to evaluate definitively the several theories by means of measurements of both moduli and extents of swelling of networks prepared under conditions carefully chosen so as to maximize the differences between the predictions of the various theories.

Theory

According to the most general versions[3,13,16] of the theory of rubberlike elasticity, the change ΔA_{el} in the Helmholtz free energy resulting from the deformation of a network of chains having a Gaussian distribu-

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(18) G. Gee, J. B. M. Herbert, and R. C. Roberts, *Polymer*, **6**, 541 (1965).
(19) A. M. Rijke and G. L. Taylor, *J. Polym. Sci.*, *Part A-1*, **5**, 1433 (1967).
(20) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.
(21) L. R. G. Treloar, "The Physics of Rubber Elasticity," Oxford University Press, London, 1958.

tion of end-to-end vectors is given by the general expression

$$\Delta A_{\mathrm{el}} = \nu kT[(^1/_2)(V/V_0)^{2/3}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2) - \omega \ln (V/V_0) - {^3/_2}] \quad (1)$$

The factor ν is the number of chains in the network,[22] k the Boltzmann constant, T the absolute temperature, and ω a constant, the magnitude of which is the point of controversy (see below). The quantity V is the volume of the network, and V_0 is the volume such that the mean-square end-to-end distance of the chains in the network is that of the free, unperturbed chains when isotropy obtains. For networks prepared at the temperature of application of eq 1, V_0 may be identified with the volume at which the network was formed. The deformation is characterized by the elongations α_x, α_y, and α_z, where each $\alpha = L/L_i$ is defined as the ratio of the dimension L of the stressed sample along the specified coordinate to the value L_i of the same dimension of the isotropic sample at volume V.[13]

In the theory of Flory and coworkers, the logarithmic term in the volume arises from the view that in deriving an expression for ΔA_{el}, one should consider all networks having the specified number of chains.[10,11] Since $\nu/2$ cross-links are required for a network to have ν chains, the random distribution of these cross-links over the sample volume gives an entropic contribution of $(\nu/2)k \ln V$. The corresponding term in eq 1 is therefore obtained by setting $\omega = {^1/_2}$. Hermans has supported the existence of such a contribution, but has criticized the method used by Flory and coworkers to evaluate its magnitude; his calculation yields the result $\omega = 1$.[16] James and Guth, however, have argued that one may simply consider a single (idealized, regular) network which approximates the actual network, and that there is therefore no basis for such a term; *i.e.*, $\omega = 0$.[6]

The elastic equation of state for any type of deformation may be obtained from the general relationships[23]

$$f = (\partial A_{\mathrm{el}}/\partial L)_{V,T} = (\partial A_{\mathrm{el}}/\partial \alpha)_{V,T}(\partial \alpha/\partial L)_{V,T} \quad (2)$$

where f is the force exhibited by the sample at length L. It is important to note that the thermodynamic restriction to constant volume eliminates any contribution from the controversial logarithmic term. For the case of uniaxial extension, $\alpha = \alpha_x$, $\alpha_y = \alpha_z = \alpha^{-1/2}$, and

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

where L_i is the length of the unstressed sample at volume V.[23,24] Variation in the cross-sectional areas of the samples may be taken into account by normalizing the force with the cross-sectional area A^* of the unswollen, unstressed sample

$$f^* = (\nu kT/L_iA^*)(V/V_0)^{2/3}(\alpha - \alpha^{-2}) \quad (4)$$

In anticipation of the restriction of the force–elongation measurements to unswollen networks and to the same temperature at which the networks were prepared, we may identify V as V^*, the volume of the unswollen, unstressed sample. The quantity V/V_0 is then simply the volume fraction $v_{2,\mathrm{C}}$ of the polymer present in the system used for the preparation of the network. The ratio of the stresses[25] f_{S}^* and f_{B}^* at equal elongations α of two samples which have been cross-linked in solution and in the bulk ($v_{2,\mathrm{C}} = 1$) state, respectively, is therefore (uncontroversially) predicted to be

$$f_{\mathrm{S}}^*/f_{\mathrm{B}}^* = (\nu v_{2,\mathrm{C}}^{2/3})_{\mathrm{S}}/\nu_{\mathrm{B}} \quad (5)$$

where the ν's are now the number of chains per unit volume. Their ratio also represents the ratio of cross-link densities and, alternatively, the "moduli" $f^*/(\alpha - \alpha^{-2})$ of the two samples.

The use of swelling equilibrium measurements to determine the cross-link densities required in eq 5 provides a basis for discriminating between the conflicting theories. If a network is placed in contact with an excess of a thermodynamically good solvent, it will absorb solvent until the increase in elastic free energy due to the three-dimensional, isotropic deformation of the network balances the decrease in free energy due to mixing polymer and solvent. The condition for swelling equilibrium is therefore[10]

$$\partial \Delta A_{\mathrm{el}}/\partial n_1)_{T,V} + (\mu_1 - \mu_1^\circ)_{\mathrm{mixing}} = 0 \quad (6)$$

where n_1 is the number of molecules of solvent, and μ_1 and μ_1° are the molecular chemical potentials of the solvent in the network and in the pure state, respectively. The first term, obtained by the indicated differentiation of eq 1, with $\alpha_x = \alpha_y = \alpha_z = 1$, is found to be

$$(\nu V_1 kT/V^{*1/3}V_0^{2/3})[v_{2,\mathrm{N}}^{1/3} - \omega v_{2,\mathrm{N}}(V_0/V^*)^{2/3}] = (\nu V_1 kT v_{2,\mathrm{C}}^{2/3}/V^*)(v_{2,\mathrm{N}}^{1/3} - \omega v_{2,\mathrm{N}} v_{2,\mathrm{C}}^{-2/3}) \quad (7)$$

where V_1 is the molecular volume of the solvent and $v_{2,\mathrm{N}}$ is the volume fraction of polymer in the network at swelling equilibrium. Adoption of the Flory–Huggins expression[26–28] for the second term of eq 6 gives for the equilibrium condition

$$(\nu V_1 v_{2,\mathrm{C}}^{2/3}/V^*)(v_{2,\mathrm{N}}^{1/3} - \omega v_{2,\mathrm{N}} v_{2,\mathrm{C}}^{-2/3} = -[\ln (1 - v_{2,\mathrm{N}}) + v_{2,\mathrm{N}} + \chi_1 v_{2,\mathrm{N}}^2] \quad (8)$$

where χ_1 is a free energy of interaction parameter of solvent with polymer.

It is thus possible in principle to determine ν for any network from knowledge of the concentration of polymer in the system in which the cross-linking was carried out, and the extent of its equilibrium swelling in a solvent for which χ_1 is accurately known. Values of χ_1 obtained from swelling equilibrium results on networks for which ν has been estimated from stress–strain measurements are unacceptable for the present purposes since they require adoption of a specific form of eq 1 for their determination. Although other techniques are available for estimating χ_1,[20] the difficulties in determin-

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(22) In the theory of James and Guth, the structure factor is not specifically given as ν, but is a complicated quantity requiring for its evaluation detailed knowledge of the structure of the network. Their estimate (ref 4) of this factor for a simple, limiting case would result in replacing ν by $\nu/2$ in eq 1, 3, and 4. Since the experimental comparison to be attempted will involve *ratios* of these factors, introduction of such a constant is inconsequential.

(23) Reference 20, Chapter XI.

(24) A. V. Tobolsky and M. C. Shen [*J. Appl. Phys.*, **37**, 1952 (1966)] have suggested a semiempirical modification of this equation of state which could alter the volume dependence shown here. Since the magnitude of the proposed effect must at the present time be obtained experimentally, it would be inappropriate to consider their equation on the same basis as eq 3.

(25) The quantity f^* is not a true stress, since the area used in its definition is not that of the sample at the existing deformation. The distinction is irrelevant for the purpose at hand.

(26) M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942); *Ann. N. Y. Acad. Sci.*, **41**, 1 (1942); *J. Amer. Chem. Soc.*, **64**, 1712 (1942).

(27) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(28) Reference 20, Chapter XII.

ing this quantity and the unanticipated concentration dependence it frequently exhibits[28] argue against this direct approach for determining the ratio of ν's required in eq 5.

The troublesome evaluation of the Flory–Huggins expression can be avoided if the two samples to be compared are cross-linked to give the same value of $v_{2,N}$ (in the same solvent and at the same temperature). The most direct way of accomplishing this is to prepare a solution of the polymer in the solvent chosen for the swelling equilibrium measurements and at a value of $v_{2,C}$ equal to the value of $v_{2,N}$ exhibited by a network of the same polymer prepared in the undiluted state. Cross-linking of the polymer in solution to the visually observable syneresis point (see below), for which $v_{2,N} = v_{2,C}$, will then provide the second of a pair of samples having equal values of $v_{2,N}$ but very different values of $v_{2,C}$. Equating the values of the left-hand side of eq 8 for these two cases and using $v_{2,N} = v_{2,C} = v_2$ for the sample cross-linked in solution and $v_{2,N} = v_2$ and $v_{2,C} = 1$ for the sample cross-linked in the undiluted state yields

$$\nu_S/\nu_B = (v_2^{1/3} - \omega v_2)/v_2(1 - \omega) \qquad (9)$$

Substitution of this relationship into eq 5 gives for the predicted ratio of the moduli at equal elongations

$$f_S^*/f_B^* = (1 - \omega v_2^{2/3})/(1 - \omega) \qquad (10)$$

According to the theory of James and Guth, $\omega = 0$ and therefore $f_S^*/f_B^* = 1$ for comparison at any value of v_2. The theory of Flory, for which $\omega = 1/2$, yields $f_S^*/f_B^* = 2 - v_2^{2/3}$; the ratio is predicted to have a maximum value of 2, for $v_2 \rightarrow 0$, and to decrease monotonically to a value of 1 as $v_2 \rightarrow 1$. Hermans' theory, which yields $\omega = 1$, leads to an impossible result because of the presence of the quantity $(1 - \omega)$ in the denominators of eq 9 and 10. The physical meaning of this result is that the syneresis point is predicted to be unattainable. Since syneresis is a well-known phenomenon,[29] the theory of Hermans can be dismissed at this point as being fundamentally incorrect.

Stress–strain measurements at constant temperature frequently depart from the form of eq 4 in that $f^*/(\alpha - \alpha^{-2})$ shows a dependence on α.[30,31] In recognition of this complication, stress–strain isotherms are almost invariably expressed according to the empirical relationship[32]

$$f^*/(\alpha - \alpha^{-2}) = 2C_1 + 2C_2\alpha^{-1} \qquad (11)$$

where C_1 and C_2 are unspecified constants, with the latter serving as a measure of the departure from the predicted form of the dependence of stress on strain. Comparison of moduli at equal elongations minimizes the effect of this complication.

Experimental Section

Preparation of Networks. The polymer used was a sample of 1,4-polybutadiene having a cis content close to 100%.[33] Its intrinsic viscosity in benzene at 30° was approximately 2.0; this corresponds to a molecular weight of 0.4×10^6,[34] according to published results[35] on this system. On the basis of pycnometry and a density-matching technique using water–methanol solutions, its density at 25° was found to be 0.9028 (±0.0004) g cm^{-3}.

The series of samples to be cross-linked in the undiluted state were obtained by pressing a sample of the polymer, at 60–65°, into a sheet having a uniform thickness of ~0.1 cm. A precision rubber die was then used to cut strips having widths of approximately 0.3 cm from this sheet; a temperature slightly above the glass transition temperature (~ −100° [35]) was used to prevent distortion of the sample during cutting. Approximately 5-cm lengths of the strips were placed between polyethylene film (~0.01 cm thick) for support and these samples were then inserted into Pyrex glass tubing (0.6-cm i.d.). The samples were degassed at room temperature for at least 12 hr in order to remove oxygen, and were then sealed under vacuum.

The solutions to be used in the preparation of the other series of networks were prepared by mixing weighed amounts of the degassed polymer and reagent grade benzene which had been purged with prepurified nitrogen for at least 1 hr. Each solution was used to fill a dozen Pyrex glass tubes (0.6-cm i.d., ~20-cm length) which contained aluminum foil liners (0.004 cm thick) to facilitate recovery of the (swollen) samples after cross-linking. The filled tubes were frozen in liquid nitrogen and then sealed under vacuum.

Both types of samples were cross-linked at 20–26°,[36] using γ radiation[37] from a ^{60}Co source having a radioactivity of ~4900 Ci. The dose rate employed was ~0.17 Mrad/hr, and doses ranged from ~4 to 114 Mrads. Samples were not opened until at least 12 hr after irradiation in order to permit decay of the free radicals generated in the samples.

Swelling Experiments. A small portion of each sample cross-linked in solution was deswelled in methanol and dried under vacuum to constant weight. These portions, along with similar, weighed portions of the samples cross-linked in the absence of solvent, were extracted with gently stirred benzene at room temperature for 24 hr, and were then deswelled and dried as already described. The fractional loss in weight was taken to represent the soluble (uncross-linked) fraction of the sample.

The remaining, main portion of each sample cross-linked in solution was placed in a large excess of nitrogen-purged benzene at room temperature for 12 hr to extract extraneous products possibly resulting from the γ irradiation of the benzene. The main portions of all of the samples, later to be used in the force-elongation measurements, were then placed in fresh, nitrogen-purged benzene at 25.00 (±0.01)° to determine their equilibrium degrees of swelling. The observed uniformity of swelling attested to the uniformity of cross-linking. Swollen samples were removed from the benzene and weighed in weighing bottles at intervals of at least 4-hr duration until the weights were constant to ±0.2%. The samples were then deswollen and dried to constant weight. The value of $v_{2,N}$ for each network was calculated from the weights of the swollen and dry networks, using the densities of the polymer and benzene[38] at 25° and assuming additivity of volumes; a similar calculation gave $v_{2,C}$.

Determination of Syneresis Points. It is of course possible to locate visually the point at which $v_{2,N} = v_{2,C}$, since if cross-linking

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(29) See, for example, ref 17 and P. Alexander and A. Charlesby, *J. Polym. Sci.*, 23, 355 (1957). Syneresis is reported in the present study as well.

(30) Typical results may be found in the literature cited in ref 31 and in Chapter VIII of ref 21.

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

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

(33) This sample, prepared at the Polymer Corp. Laboratories (Sarnia, Canada), was generously provided by Dr. H. L. Williams.

(34) Use of a polymer of high molecular weight facilitates cross-linking and also permits neglect of a correction to the elastic equation of state arising from the fact that terminal portions of the chains do not contribute to the elastic response (ref 9).

(35) J. Brandup and E. H. Immergut, Ed., "Polymer Handbook," Interscience, New York, N. Y., 1966.

(36) The temperature during most of the irradiation was 25 (±1)°; a mechanical malfunction caused a decrease in temperature to 20° for a relatively short period of time. The resulting small uncertainty in the volume at which the cross-linking occurred is of negligible importance.

(37) In addition to forming chemical cross-links between the chains, the γ radiation can cause geometric isomerization of the double bonds in the chain backbone and, in the case of benzene solutions, some phenylation of the polymer: M. A. Golub, *J. Amer. Chem. Soc.*, 82, 5093 (1960); *J. Phys. Chem.*, 69, 2639 (1965). According to theory, this should have no effect on the elastic equation of state because of its universal character. The effect on the cross-link density estimated from eq 8 should be small because such structural changes should not drastically change χ_1 for the system, and ν should not be markedly sensitive to χ_1 in the case of a polymer in a thermodynamically good solvent.

(38) R. R. Dreisbach, "Physical Properties of Chemical Compounds," American Chemical Society, Washington, D. C., 1955.

Table I. Sample Characteristics and Stress–Strain Data

Sample	$v_{2,C}$	Radiation dose, Mrads	Soluble fraction	$v_{2,N}$	$f^*/(\alpha - \alpha^{-2})$,[a] kg/cm^2	$2C_2$, kg/cm^2	Av time required for equilibrium, hr	$\left[\frac{f^*(\text{equil})}{f^*(\text{init})}\right]_{\text{av}}$	$\frac{L_i(\text{after})}{L_i(\text{before})}$
B1	1.000	3.50	0.230	0.05615	1.87	2.09	3.89	0.765	1.033
B2	1.000	4.33	0.159	0.07341	1.93	1.96	2.95	0.803	1.019
B3	1.000	5.23	0.107	0.09013	2.13	1.57	2.97	0.847	1.012
B4	1.000	6.13	0.096	0.1029	2.36	1.79	2.27	0.886	1.013
S1	0.05511	65.3	0.023	0.05505	0.899	0.221	0.73	0.959	1.002
S2	0.06984	77.7	0.032	0.06913	1.15	0.425	0.51	0.989	1.001
S3	0.08397	102.1	0.014	0.08411	1.44	0.414	0.44	0.989	1.005
S4	0.1005	114.4	0.006	0.1005	2.01	0.927	0.26	0.997	0.999

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

is continued beyond this point, the system undergoes syneresis; *i.e.*, it separates into two phases, the swollen network having $v_{2,N} > v_{2,C}$ and the pure solvent. Visual determination of this (incipient) syneresis point is not very accurate, however, and is inconvenient in cases where the cross-linking is done with high-energy radiation because of the safety precautions required. In the method employed here, the extent of equilibrium swelling $v_{2,N}$ was studied as a function of radiation dose for each of the solutions. Interpolation of such data immediately gives the dose required to reach the syneresis point for each solution concentrated $v_{2,C}$.

Force-Elongation Measurements. The apparatus consisted of a glass cell in which the sample was to be mounted between two clamps, one attached to the bottom of the cell and the other connected to a movable force transducer (Statham Model G1-16-350) run by a constant voltage, dc power supply (Hewlett-Packard Model 6217A). The output from the transducer was displayed on a recorder (Leeds and Northrup, Model Speedomax W Azar) and was calibrated using a set of standard balance weights. The cell was thermostated at 25.00 (±0.05)°, and during sample elongations was swept with an inert atmosphere of prepurified nitrogen.

Test sections approximately 3 cm long were demarcated on the central part of each sample by insertion of two short lengths of thin copper wire (0.016-cm diameter) while the sample was in the highly swollen state (to minimize damage to the network). The samples which had been cut from a sheet had thin, rectangular cross sections and could easily be clamped. The samples prepared in solution, however, were difficult to clamp directly because of their circular cross sections (~0.20–0.27-cm diameter); they were therefore glued with epoxy cement to metal tabs which were held by the clamps.

A stress–strain isotherm was obtained for each sample by the following procedure. The sample, in the unswollen state, was mounted in the cell and the unstressed length L_i of the test section measured to ±0.002 cm by means of a cathetometer (Pye Model 6166). The sample was then elongated to the desired length and the force was monitored until it remained sensibly constant for at least 0.25 hr. This was considered to be the equilibrium value of the force; it was recorded, along with the length of the sample and the time required for this equilibrium condition to be reached. A series of measurements at five or more elongations, consecutively increasing from $\alpha \cong 1.2$ to 1.7, were carried out in this manner. After the sample was permitted to recover under zero force for at least 12 hr, its unstressed length was remeasured and used to calculate the precise values of α, and its cross-sectional area A^* was measured using a micrometer and cathetometer. The extent of equilibrium swelling of one of the samples was then remeasured to determine if any chain scission had occurred as a result of the stress–strain experiments.

Results

Four samples were prepared by cross-linking the polymer in bulk ($v_{2,C} = 1.000$); they were labeled B1–4 and are described in the first four rows of Table I. Low radiation doses, listed in column three, were used, since eq 10 indicates that the difference between the theoretical predictions is maximized at low degrees of cross-linking. As a result, values of the fraction of soluble material in these samples, given in column four, are rather high. As expected, the values of $v_{2,N}$, given in column five, are relatively low.

Networks were also prepared from four solutions of the polymer in benzene, at concentrations ranging from $v_{2,C} \cong 0.055$ to 0.10. (Lower concentrations are unsuitable because of the difficulty of getting enough intermolecular cross-linking for network formation. A significantly higher concentration would give a solution which would be difficult to handle because of its very high viscosity and would require an impractically high radiation dose to reach its syneresis point; furthermore, a sample prepared under these conditions would have a sufficiently high cross-link density to make measurement of its stress–strain isotherm difficult.) Figure 1 shows the volume fraction of polymer at swelling equilibrium in benzene at 25° as a function of radiation dose for networks formed from each of the solutions. The observed increase in $v_{2,N}$ with increasing $v_{2,C}$ at constant radiation dose is due to the dependence of $v_{2,N}$ on ν shown in eq 8 and the increase in efficiency of cross-linking as $v_{2,C}$ increases. The marked curvature in one of the plots is unimportant for the purpose of the experiment; the solution to which it pertains may simply have differed slightly from the others in the extent to which oxygen had been successfully excluded. The intersection of each curve with the arrow corresponding to its value of $v_{2,C}$ establishes the radiation dose required to reach the syneresis point for that solution.

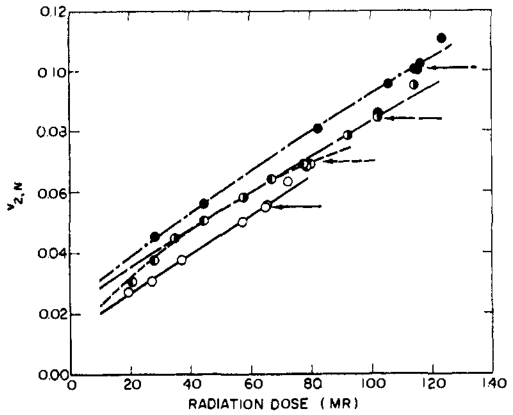

Figure 1. The volume fraction $v_{2,N}$ of polymer at swelling equilibrium in benzene at 25° *vs.* radiation dose for networks of *cis*-1,4-polybutadiene prepared from solutions having volume fractions $v_{2,C}$ of polymer of 0.05511 (○), 0.06984 (◐), 0.08397 (◑), and 0.1005 (●).

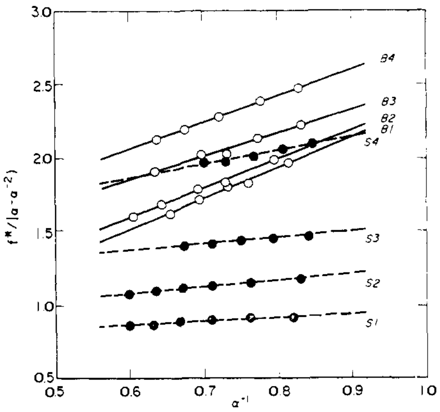

Figure 2. The dependence of the modulus $f^*/(\alpha - \alpha^{-2})$ in kg cm^{-2} on the reciprocal elongation for the undiluted networks at 25°.

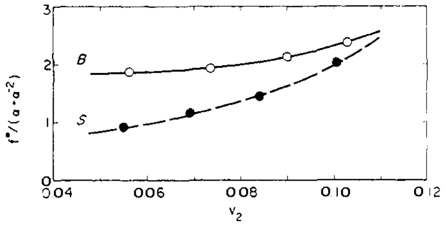

Figure 3. The modulus at an elongation of α = 1.300 as a function of the volume fraction v_2 of polymer at swelling equilibrium in benzene at 25° for networks cross-linked in the bulk state (curve B) and in solution to the syneresis point (curve S).

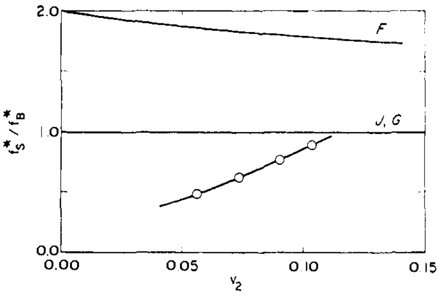

Figure 4. The ratio of the moduli of Figure 3, at equal v_2, as a function of v_2. The lines labeled J,G and F represent the theoretical predictions of James and Guth and Flory, respectively.

(Points corresponding to synerized samples, those having $v_{2,N} > v_{2,C}$, invariably lie above the curve determined by points for which $v_{2,N} \leqslant v_{2,C}$. This is due to the increased efficiency of cross-linking resulting from the increase in polymer concentration in the network as it exudes solvent.)

Several samples of each solution were irradiated to this specified dose and swelling equilibrium measurements were used to determine which network from each solution most nearly meets the condition $v_{2,N} = v_{2,C}$. The four samples thus chosen were designated S1–4 and are described in the lower part of Table I. The radiation doses required to reach the syneresis point, given in column three, are quite high because the efficiency of cross-linking in systems containing large amounts of diluent is low and, as shown by eq 9, many more cross-links must be introduced in such cases to give a network having the same equilibrium degree of swelling as one cross-linked in the absence of diluent. The high degree of cross-linking is the reason for the very low values of the fraction of soluble material measured for these samples and recorded in column four. Values of $v_{2,N}$ are given for each sample in the following column; their agreement to within a few tenths of a per cent with the values of $v_{2,C}$ listed in column two shows that the attempt to cross-link these samples precisely to the syneresis point was successful.

The normalized forces f^*, expressed in kg/cm^2 of unswollen, unstressed cross-sectional area, were divided by the strain function $\alpha - \alpha^{-2}$ and, as suggested by eq 11, were plotted against α^{-1}. The results, shown in Figure 2, were well represented by straight lines, the locations of which were determined by least-squares analysis. Interpolation was used to obtain values of the modulus $f^*/(\alpha - \alpha^{-2})$ at α = 1.300, an elongation large enough to minimize the effect of uncertainties in measuring the unstressed length of a sample, but small enough to avoid non-Gaussian deviations in the elastic equation of state. These values are listed in column six of the table, with values of the slope of each line, $2C_2$ in eq 11, given in the following column.

The time required for mechanical equilibrium to be established in an elongated network is a measure of the amount of noninstantaneous chain motion occurring as a result of the imposed stress. Values of this quantity, averaged over the set of elongations of each sample, are given in column eight of the table. The similarly averaged extent of relaxation of the stress, the ratio of the value of the force at equilibrium to its value immediately upon elongation of the sample, is listed in the following column. The final column records the permanent distortion of each sample, expressed as the ratio of the value of the unstressed length upon completion of all elongations to its initial value, before any stresses were imposed. The sample, B1, exhibiting this relaxation behavior most strongly was found to have the same equilibrium swelling before and after the elongations; this rules out chain scission as a significant contributor to these effects.

Comparison of theory with experiment as suggested by eq 10 requires ratios of the moduli for unswollen samples which give the same value of v_2 when swollen in benzene. Values of these ratios were obtained from the results of Table I by the two plots of $f^*/(\alpha - \alpha^{-2})$ *vs.* v_2 shown in Figure 3. Interpolation was used to obtain moduli for the samples cross-linked in solution at the values of v_2 found for the samples cross-linked in the bulk state. The ratios of the moduli of the two types of sample, at equal v_2, along with the theoretical predictions of James and Guth, and Flory, are given in Table II and are shown as a function of v_2 in Figure 4.

Table II. Values of f_S^*/f_B^*

v_2	Exptl[a]	Calcd James, Guth	 Flory
0.05615	0.482	1.000	1.853
0.07341	0.622	1.000	1.825
0.09013	0.765	1.000	1.799
0.1029	0.888	1.000	1.780

[a] α = 1.300.

Neither theory is successful in predicting the observed magnitude of the ratio or its dependence on v_2.

Discussion

It is important to note that no reasonable adjustment of the volume-dependent term in the entropy by modification of the value of ω in eq 10 will give agreement between theory and experiment. A negative value of ω would be required and this is clearly impossible, since it would correspond to an entropy contribution which would decrease as the volume of the system increased.

A basis for understanding the observed discrepancies probably resides in the several marked differences in properties between the two types of networks. As shown in Table I, those cross-linked in solution have considerably smaller values of the empirical $2C_2$ correction to the predicted stress–strain relationship, even at equal values of the modulus. Alternatively, some workers[39] use the ratio C_2/C_1 as a measure of this correction which approximately takes into account the fact that C_2 appears to increase with increasing modulus.[31] This normalized correction differs even more strikingly for the two types of samples: for the networks cross-linked in the undiluted state, values range from 1.71 to 8.10 and average 4.06, while for those cross-linked in solution the range is 0.30 to 0.71, with an average of 0.47. Thus, networks formed in solution approach much more closely the stress–strain dependence predicted in the theoretical elastic equation of state. Allen[40] has recently reached the same conclusion for networks prepared from natural rubber. Furthermore, as is obvious from the last three columns of Table I, these samples also require considerably less time to reach mechanical equilibrium and exhibit much less stress relaxation and permanent deformation.

A consistent explanation of these observations can be found in the assumption underlying all of the present theories, namely that the chains in a network can readily pass through one another, in that they are allowed all configurations in the adoption of the Gaussian distribution function. According to this idealization, the network segments shown in Figure 5, each of which consists of four chains of equal contour length and end-to-end distance, are all entirely equivalent. Segment b, which contains a temporary chain entanglement, would differ from a in its instantaneous elastic response but not in its equilibrium retractive force. Segment c, however, which contains a permanent entanglement, would probably differ from a and b in both respects. Of crucial importance is the reasonable expectation that the difference observed should depend on the *type* of deformation as well as its extent. This leads to the serious complication that, for example, an estimate of cross-link density using a swelling equilibrium experiment (which involves a three-dimensional, isotropic deformation) may not be directly applicable in the interpretation of a uniaxial extension of the same network.

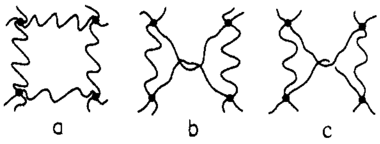

Figure 5.

The magnitude of the error committed by assuming the general applicability of a single type of estimate of the cross-link density would depend markedly on the topological complexity of the network, as measured, for example, by its number of permanent chain entanglements. As is obvious from the observed values of the $2C_2$ correction and the extent of relaxation effects, the two types of networks studied here have very different topologies, and thus the magnitude of the error involved in neglecting the above complication would also be expected to be quite different for the two cases. Cross-linking in solution, for example, may produce regions which have a high density of cross-links and entanglements but a relatively low degree of bonding and entanglement with the rest of the network. Such inhomogeneities would be effective in suppressing the degree of swelling but would contribute little to the elastic retractive force in uniaxial extension. Such an effect could be the basis for the low values of f_S^*/f_B^* observed in the present study.

As has been pointed out previously, successful revision of the theory of polymer networks will undoubtedly require abandonment of the representation of a network as a collection of "phantom" chains capable of freely passing through one another.[41–43] A completely adequate theory must explicitly take into account the topology of the network structure.

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(39) See, for example, T. L. Smith, *J. Polym. Sci., Part C*, **16**, 841 (1967).

(40) G. Allen, private communication.

(41) M. J. Voorn and J. J. Hermans, *J. Polym. Sci.*, **35**, 113 (1959).

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