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(13) Flory, P. J. *Macromolecules* **1979**, *12*, 119.
(14) The present theory is not applicable as it stands to networks formed in states of strain such that the configurations of the chains are not random and not isotropically distributed.
(15) Calculations presented previously[1,13] for $p > 2$ are in error owing to omission of the terms of eq 19 and 24 that involve the quantity $(\eta_0/\eta_\lambda)(\sigma_\lambda/\sigma_0) - 1$. These terms vanish only when $(\sigma_0/\sigma_\lambda) = \eta_0/\eta_\lambda$. The omission does not seriously vitiate the calculations presented previously[1,13] for $\eta_0/\eta_\lambda = \lambda^2$ and $\sigma_0/\sigma_\lambda = \lambda^p$ with $p > 2$. This error is avoided in the present rendition. We are grateful to Dr. R. W. Brotzman and Professor B. E. Eichinger[16] for turning our attention to the omission of this term.
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Relationships between Stress, Strain, and Molecular Constitution of Polymer Networks. Comparison of Theory with Experiments

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ABSTRACT: The theory recast in the preceding paper accounts for the relationship of the equilibrium stress to strain for elastomeric networks within probable limits of experimental error throughout the range of deformation accessible to experiment, including biaxial extension, pure shear, and torsion as well as simple elongation and compression. Effects of dilation by swelling on the stress–strain relationship are well reproduced by the same set of parameters: the reduced force $[f^*_{ph}]$ for the equivalent phantom network, and κ and ζ that characterize the local constraints on fluctuations of junctions and their dependence on strain. Two of these three parameters appear to be related by $\kappa[f^*_{ph}]^{1/2}$ = const, as follows from the premise that κ should depend on the degree of interpenetration in the network. Values of $[f^*_{ph}]$ deduced from elastic and swelling measurements agree approximately with "chemically" determined reduced forces given by $\xi kT/V^0$. It follows that one of the parameters is determinable independently and that discrete ("trapped") entanglements do not contribute appreciably to the stress.

Introduction

Experimental results on (i) the relationship of stress to strain, (ii) the effect of dilation on the stress–strain relationship in simple extension, and (iii) the effect of the degree of cross-linking on the form of this relationship are examined in this paper according to the theory presented in the preceding one.[1] For the interpretation of (iii), we introduce the physically plausible postulate that the parameter κ should be proportional to the degree of interpenetration in the network.

Most of the experimental results treated below pertain to uniaxial deformations. They are presented in terms of the reduced force, or reduced nominal stress, defined by

$$[f^*] = f^*(V/V^0)^{-1/3}(\alpha - \alpha^{-2})^{-1} \qquad (1)$$

where f^* is the tensile force per unit area measured in the reference state, V^0 is the volume in that state, V is the volume of the system at measurement, and α is the extension ratio relative to the length of the sample when isotropic at the same volume V. According to theory,[1,2]

$$[f^*] = [f^*_{ph}](1 + f_c/f_{ph}) \qquad (2)$$

where f_c is the contribution to the force f from the constraints on fluctuations of junctions,[1,2] f_{ph} is the force that would be exerted by the equivalent phantom network at the same elongation, and $[f^*_{ph}]$ is the reduced force in the limit of high extension (and/or dilution) where f_c/f_{ph} vanishes. Thus, $[f^*_{ph}]$ is the reduced force for the equivalent phantom network.

According to theory,[2,3]

$$[f^*_{ph}] = \xi kT/V^0 \qquad (3)$$

where ξ is the cycle rank of the network; see eq 42 of the preceding paper.[1] Implicit in identification of ξ with the value that follows directly from the chemical constitution of the network is the assumption that the effective degree of connectivity is not enhanced by discrete entanglements[1] of the kind often assumed to entwine one chain of the network specifically with another. Specific entanglements of this kind are to be distinguished from the diffuse entanglements addressed by the theory[1,2] under consideration. In the fourth section below, we examine the validity of eq 3 by comparing values of $[f^*_{ph}]$ deduced according to eq 2 from stress–strain–swelling measurements with those calculated from chemically determined "circuit densities" ξ/V^0.

Dependence of Stress on Strain

Stresses for uniaxial deformation covering a wide range of extension ratios α can be determined by combining measurements in simple extension with measurements on the inflation of a sheet of the rubber.[4-7] The latter experiments require measurement of the inflation pressure, of the radius of curvature at the pole of the inflated sheet, and of the linear deformation in the plane of the sheet and likewise at the pole. The strains may be expressed either as equibiaxial extensions or, preferably for purposes at hand, as uniaxial compressions. Measurements in compression and in elongation should be performed on samples from the same specimen of rubber.

Rivlin and Saunders[6] applied this procedure to vulcanized natural rubber. Their measurements in extension cover the range from α = 1.1 to 3, and in compression from α = 0.85 to 0.14, i.e., equibiaxial extensions from $\alpha_2 = \alpha_3$ = 1.08 to 2.6. Similar experiments were reported a few years ago by Pak and Flory[7] on networks of poly(dimethylsiloxane), PDMS, cross-linked using dicumyl peroxide at 165 °C. The experiments covered a fourfold range

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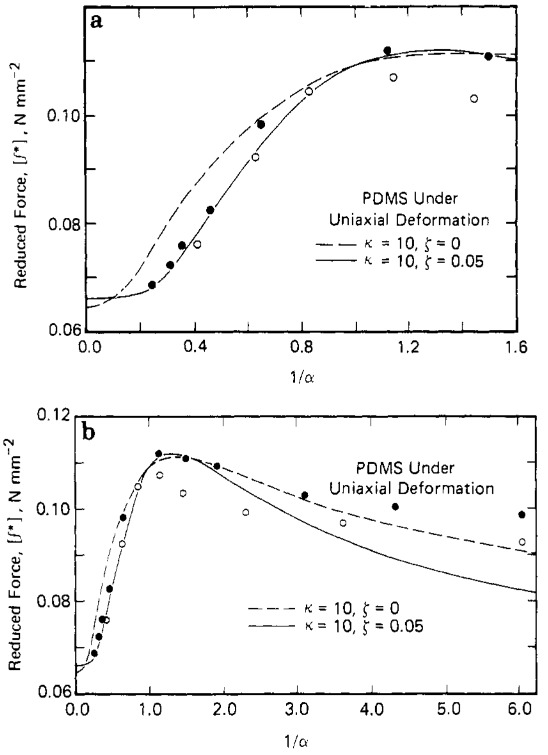

Figure 1. Reduced force for a PDMS network as a function of the reciprocal of the extension ratio α for uniaxial extension ($\alpha^{-1} < 1$) and for uniaxial compression ($\alpha^{-1} > 1$). The filled circles represent experimental measurements[7] taken in the order of increasing extension or compression; open circles were measured in the opposite orders. The dashed curve was calculated according to theory[1] with $\kappa = 10$ and $\zeta = 0$, the solid line with $\kappa = 10$ and $\zeta = 0.05$. Figure 1a details results in extension but includes those in compression for $1 < \alpha^{-1} < 1.6$. Figure 1b covers the entire range up to $\alpha^{-1} \simeq 6$, with emphasis on measurements in compression.

of extension and a sixfold range in compression, both sets of experiments being conducted on samples from the same specimen. Thus, the combined range is 24-fold, from $\alpha = {}^1/_6$ to 4. Because of complications of crystallization in the experiments[6] on natural rubber, we compare theory with the experiments on PDMS. As Pak and Flory[7] showed, however, the results for the two polymers are similar, apart from deviations attributable to crystallization of the natural rubber at high strains.

The results for PDMS are compared with theory in Figures 1a and 1b where the reduced forces are plotted against α^{-1}. The former figure emphasizes the range of extension, $\alpha^{-1} < 1$, but includes also the lower range of compression up to $\alpha^{-1} = 1.6$. Figure 1b emphasizes the range of compression but includes results for extension, albeit on a reduced scale. The curves have been calculated according to eq 37, 40, and 43 of the preceding paper in conjunction with eq 2 above. Values of the parameters for the dashed and solid curves, respectively, are $\kappa = 10$, $\zeta = 0$ and $\kappa = 10$, $\zeta = 0.05$. The intercepts $[f^*_{\mathrm{ph}}]$ have been so chosen as to render the reduced forces equal at $\alpha = 1$. The quantity μ/ξ was set equal to unity in these and in other calculations below on the assumption that the various networks treated here may be considered to be perfect, tetrafunctional ones.[1,2] The solid curve calculated with the nonzero, small value assigned to ζ affords the better fit to the experimental data for $\alpha^{-1} < 1$ but falls below the data for compression ($\alpha^{-1} > 1$). Better agreement is achieved in the latter range by taking $\zeta = 0$, but at the expense of a poorer fit for $\alpha^{-1} < 1$.

It will be observed that the open circles in Figure 1b, representing measurements taken in the order of decreasing compression α^{-1}, fall considerably below those taken with increasing α^{-1} shown by filled circles. The evident hysteresis was accentuated by the comparatively low degree of cross-linking that was required in order to encompass the widest possible range of strains without rupture of the specimen. The experiments in compression achieved by inflation of a sheet are difficult[6,7] and high accuracy cannot be claimed. Mean values between the filled and open circles probably afford the best estimates of the reduced forces at equilibrium at high compressions.

Differences between theory and experiment are comparatively small, the divergences noted notwithstanding. Even at the extremes, departures from the dashed curves at small α^{-1} in Figure 1a and from the solid curve at large α^{-1} in Figure 1b amount to only about 15%. In judging these disparities, one should note that the quantity plotted as ordinate in this figure (and in the following figures as well) is the *reduced* force. The significant range of tensile forces measured in extension is about 8-fold; in compression, it is 30-fold. A deviation of only 15% between theory and experiment over the combination of these two ranges is remarkably small.

The earlier version of the theory,[2] equivalent to the present one[1] with $\zeta = 0$, has been compared by one of us[8] with the results of Jones and Treloar[9] on natural rubber under biaxial strain, α_2 and α_3 being varied separately. The experimental results are expressed as the derivatives $\partial\Delta A_{\mathrm{el}}/\partial I_1$ and $\partial\Delta A_{\mathrm{el}}/\partial I_2$ of the elastic free energy with respect to the first and second invariants I_1 and I_2 of the strain. Values of these derivatives calculated[8] from the theory with $[f^*_{\mathrm{ph}}] = 0.4$ N mm^{-2} and $\kappa = 5$ are in good agreement with observations over wide ranges of I_1 and I_2. As was emphasized by Jones and Treloar,[9] both the classical theory of rubber elasticity and the Mooney-Rivlin formulation are utterly irreconcilable with their results.

The theory was similarly applied[8] to the measurements of Rivlin and Saunders[6] on natural rubber in pure shear superimposed on simple extension, and under combined torsion (of a cylinder) and simple extension. Good agreement was likewise achieved through arbitrary choice of $[f^*_{\mathrm{ph}}] = 0.4$ N mm^{-2} and $\kappa = 3$ for the specimens of rubber used in these experiments. Again, previous theories are inapplicable.

The possibility of refining the analysis of the foregoing results for multiaxial strains through adjustment of the parameter ζ included in the current formulation[1] is a matter under investigation. Even without the benefit of this refinement, it is evident that the theory reproduces, with remarkable accuracy, the relationship of stress to strain throughout the full range and diversity of strains accessible to experiment.

Effect of Swelling on the Stress-Strain Relationship

The results of Allen et al.[10] on natural rubber cross-linked thermally with dicumyl peroxide are shown in Figure 2. Samples were swollen with *n*-decane to varying degrees and the tensile force was measured at various extensions α. The results expressed as the reduced forces are plotted against α^{-1}. The volume fraction $v_2 = V^0/V$ in the swollen sample is indicated with each set of data. All of the curves shown in Figure 2 have been calculated as described above using a single set of parameters, namely, $[f^*_{\mathrm{ph}}] = 0.166$ N mm^{-2}, $\kappa = 8$, and $\zeta = 0.12$. The dependence of stress on strain and the influence of dilation thereon are well reproduced by the theory, except for the results at the lowest volume fraction of rubber. It is noteworthy that the reduced forces observed at this highest degree of dilation fall below the common intercept $[f^*_{\mathrm{ph}}]$

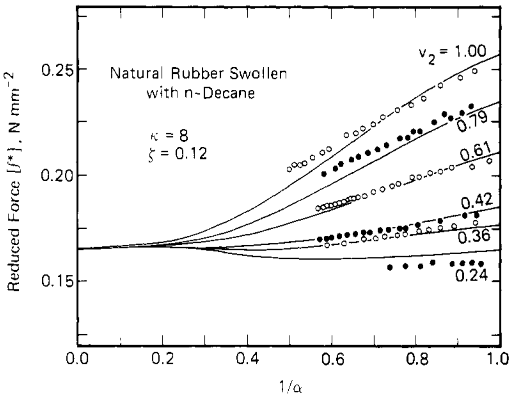

Figure 2. Reduced forces as functions of α^{-1} for natural rubber swollen to varying degrees with *n*-decane. The points represent experimental results of Allen et al.[10] for specimens of their sample B swollen to the extents indicated by the volume fractions v_2 of rubber included with each set of data. The curves were calculated according to theory with κ = 8 with ζ = 0.12.

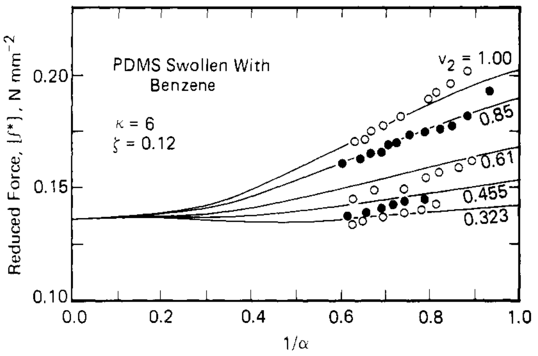

Figure 3. Reduced forces for PDMS networks swollen with benzene vapor at fixed activities plotted against α^{-1}.[11] Degrees of swelling are indicated by the volume fractions v_2 of polymer for each set of data. Curves were calculated with κ = 6 and ζ = 0.12.

as the curve calculated according to theory requires.

Results of Flory and Tatara[11] on PDMS cross-linked with electron radiation are shown in Figure 3. Samples were swollen with benzene vapor maintained at various fixed activities. The resulting volume fractions v_2 of polymer are indicated with each set of data in the figure. The curves were calculated for $[f^*_{\rm ph}]$ = 0.136 N mm^{-2}, κ = 6, and ζ = 0.12. Experimental errors are greater than for the results of Allen et al.[10] on natural rubber owing, no doubt, to the difficulties attending measurements conducted at controlled activities of vapor. The results are satisfactorily reproduced by theory, within limits of experimental accuracy. Again, reduced forces measured at the highest dilation fall below the intercept, $[f^*_{\rm ph}]$, in agreement with theory.

The results cited demonstrate that the theory is applicable to strains involving dilation as well as to those that are confined (essentially) to distortions at constant volume. Experiments[12,13] on the "elastic" contribution to the chemical potential of a volatile diluent with which a cross-linked network is swollen lend further support to this conclusion.[14]

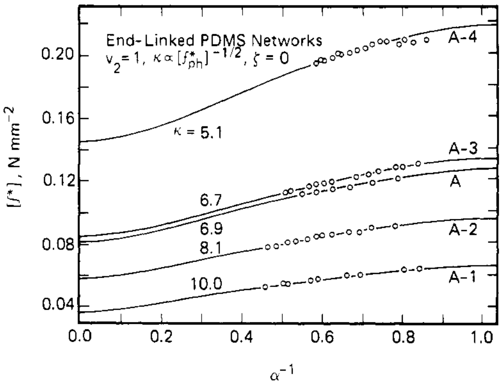

Figure 4. Results of Mark and Sullivan[15] for end-linked PDMS networks formed from linear chains of various molecular weights M_c. Samples are identified by the designation used by those authors. Values of κ were chosen to be inversely proportional to the square roots of the respective intercepts $[f^*_{\rm ph}]$.

Effect of the Degree of Cross-Linking

In the hypothetical absence of elastic constraints due to primary network connections, the variance of the fluctuation of a junction about the center of its domain of entanglement constraints would be proportional to σ_0^{-1}, according to theory, in the state of reference. The ideas elaborated in preceding papers[1,2] suggest that these fluctuations should diminish with the degree of interpenetration. Additionally, they may be scaled dimensionally to the variance $\langle(\Delta R)^2\rangle$ of the junction locations in the phantom network. The latter quantity being proportional to ρ^{-1} (see eq 4 of the preceding paper), we may expect $\kappa = \sigma_0/\rho$ to be proportional to the degree of interpenetration.

The size of the spatial domain pervaded by a given junction and the chains directly connected to it is appropriately taken to be on the order of $\langle r^2\rangle_0^{3/2}$, where $\langle r^2\rangle_0$ is the mean-square length of an unperturbed chain. The average number of junctions in a volume of this size is a proper measure of the degree of interpenetration. On the basis of the arguments presented in the preceding paragraph, we therefore suggest that

$$\kappa = I\langle r^2\rangle_0^{3/2}(\mu/V^0) \tag{4}$$

where I is the constant of proportionality and μ is the number of junctions in the volume V^0 of the state of reference. Confining attention to tetrafunctional networks for which μ may be replaced by ξ, we have

$$\kappa = I(\langle r^2\rangle_0/M)^{3/2}M_c^{3/2}\xi/V^0 \tag{5}$$

The ratio of $\langle r^2\rangle_0$ to the molecular weight M may be treated as a constant for a given polymer series in the relevant range of molecular weights; M_c is the number-average molecular weight of a chain of the network under consideration. For a tetrafunctional network

$$M_c = V^0 N_A d/2\xi \tag{6}$$

where N_A is Avogadro's number and d is the density. Hence,

$$\kappa = I(N_A d/2)^{3/2}(\langle r^2\rangle_0/M)^{3/2}(\xi/V^0)^{-1/2} \tag{7}$$

$$= I(N_A d/2)^{3/2}(\langle r^2\rangle_0/M)^{3/2}(kT/[f^*_{\rm ph}])^{1/2} \tag{8}$$

For networks (tetrafunctional) formed from polymers of a given kind, κ may be expected, therefore, to vary inversely as the square root of the reduced force in the "phantom network" limit.

In Figure 4, we show the results of Mark and Sullivan[15] on PDMS networks prepared by end-linking linear polymers terminated with hydroxyl groups, tetraethyl orthosilicate being used for this purpose. The linear polymers had been fractionated to reduce their molecular weight ranges. Their number-average molecular weights varied from 9500 to 45 000. The curves in Figure 4 were calculated by using values of κ, indicated with each curve, that vary inversely with the square roots of the respective intercepts; ζ was set equal to zero throughout. The agree-

Table I
Summary of Parameters for PEA Networks

sample	$(V/V^0)^{1/3}$ in BEE	κ	ζ	$[f^*_{\rm ph}]$, N mm^{-2}	$\kappa[f^*_{\rm ph}]^{1/2}$
E-5	1.44	1.8	0.00	0.258	0.91
E-4	1.66	2.0	0.00	0.204	0.90
E-3	1.81	7.0	0.05	0.119	2.4
E-1	2.06	16.0	0.10	0.024	2.5

ment is satisfactory. Definitive conclusions on the form of the fit (and specification of ζ) would require measurements on swollen specimens of the same samples.

Results of Erman et al.[16] for networks of poly(ethyl acrylate), PEA, prepared by quantitatively cross-linking a polymer of very high molecular weight with 1,12-diaminododecane are compared with theoretical calculations in Figure 5. Data for four samples differing in degree of cross-linking are shown. Filled circles give the reduced forces for unswollen samples; open circles represent samples swollen to equilibrium in bis(2-ethoxyethyl) ether, BEE. Measurements on all swollen specimens and on unswollen E-3, E-4, and E-5 were carried out at 25 °C. Attainment of equilibrium in unswollen samples of the lower degrees of cross-linking proved difficult owing to proximity to the glass transition, −22 °C. The measurements shown for unswollen sample E-1, not published previously, were therefore carried out at 80 °C. Equilibration was incomplete even at this temperature, as is shown by the disparity between the half-filled points taken in order of decreasing elongation and the filled points taken with increasing elongation. Results for unswollen sample E-3, determined at room temperature, are subject to error on this score as well.

Pertinent quantities and parameters for the PEA samples are summarized in Table I. The linear dilation at swelling equilibrium is given in the second column. The third and fourth columns record the parameters κ and ζ used to calculate the pair of curves shown in Figure 5 for each sample, unswollen and swollen. The common intercept for each pair of curves is given in the fifth column, and the product $\kappa[f^*_{\rm ph}]^{1/2}$ in the last column. The latter quantity is much larger for samples E-3 and E-1 than for the other two of higher degrees of cross-linking. The difference reflects the larger values of κ chosen for E-3 and E-1. Since the choice of κ was dictated principally by the reduced forces for the undiluted samples, failure to approach equilibrium may have been responsible for the difference between values appearing in the last column of Table I for samples of high and of low degrees of cross-linking. The results on PEA therefore are indecisive on the relationship of κ to the degree of cross-linking. The intercepts, which depend predominantly on the measurements on swollen samples, are believed to be accurate, however.

Calculations of interpenetration parameters I for the several rubbers treated here are summarized in Table II. Characteristic ratios $C_\infty = \lim_{n\to\infty} (\langle r^2\rangle_0/nl^2)$ taken from the sources cited are given in the second column and the quantities $(\langle r^2\rangle_0/M)N_{\rm A}$ calculated from them are given in the third column. Values of $\kappa[f^*_{\rm ph}]^{1/2}$ from the results above are included in the penultimate column. The data are too few for conclusions on the possible universality of I.

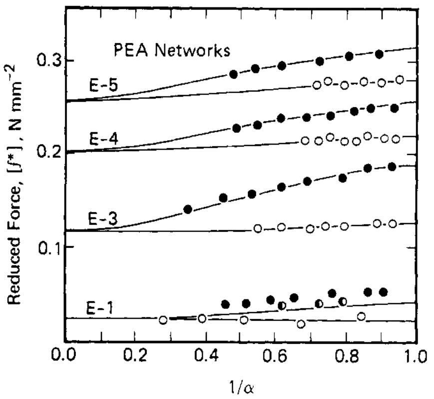

Figure 5. Results of Erman et al.[16] for poly(ethyl acrylate) networks of various, chemically determined degrees of cross-linking. Filled circles represent experimental data for unswollen samples; open circles are for swollen samples. The half-filled circles for sample E-1 were taken in the order of decreasing tension. Parameters are given in Table II.

Dependence of Observed Intercepts $[f^*_{\rm ph}]$ on Chemical Degrees of Cross-Linking

If the effective degree of interlinking is enhanced by discrete entanglements,[1] the values of $[f^*_{\rm ph}]$ deduced from elasticity measurements in the foregoing manner must reflect this increase. Comparison of $[f^*_{\rm ph}]$ with "chemical" values of $\xi kT/V^0$ (see eq 3) should be informative on this issue.

Limiting values of the reduced forces, $[f^*_{\rm ph}]$, for the end-linked PDMS networks investigated by Mark and Sullivan[15] are compared with $\xi kT/V^0 = RTd/2M_{\rm c}$ in Figure 6. The filled circles represent values of $[f^*_{\rm ph}]$ obtained from elasticity measurements by extrapolation to $\alpha^{-1} = 0$ according to the procedure demonstrated in Figure 4. The values of $\xi kT/V^0$ plotted on the abscissa were evaluated from the number-average molecular weights[15] $M_{\rm c}$ of the linear chains from which the networks were prepared. The first five filled circles represent the interecepts of the curves in Figure 4. The last two points represent limiting reduced forces similarly evaluated from the results of Mark and Sullivan[15] for their samples B-1 and B-2 of higher degrees of cross-linking (lower $M_{\rm c}$'s). The relationship described by these seven points is approximately linear, but the points are consistently above the line $[f^*_{\rm ph}] = \xi kT/V^0$ drawn in this figure. These data suggest a finite intercept. It is small, however, being only ca. 0.02 N mm^{-2}.

Mark and Sullivan[15] also measured the degrees of swelling of their networks in benzene at equilibrium. These results offer an alternative way of determining $[f^*_{\rm ph}]$.

Table II
Interpenetration Parameters for Various Rubbers

polymer	C_∞	$10^{-7}(\langle r^2\rangle_0/M)N_{\rm A}$, cm^2 g^{-1}	d, g cm^{-3}	$\kappa[f^*_{\rm ph}]^{1/2}$, N$^{1/2}$ mm^{-1}	I
PDMS[11]	7.8[17]	3.2	0.97	2.2	0.56
PDMS[15]	7.8[17]	3.2	0.97	1.95	0.50
natural rubber[9,10]	4.7[18]	3.6	0.91	2.25, 3.25[b]	0.53, 0.76[b]
PEA[16]	8.5[a]	2.4	1.09	0.9-2.4	0.3-0.8

[a] Inferred from experimental determinations on poly(methyl acrylate); see ref 19. [b] From results of Jones and Treloar[9] and of Allen et al.,[10] respectively.

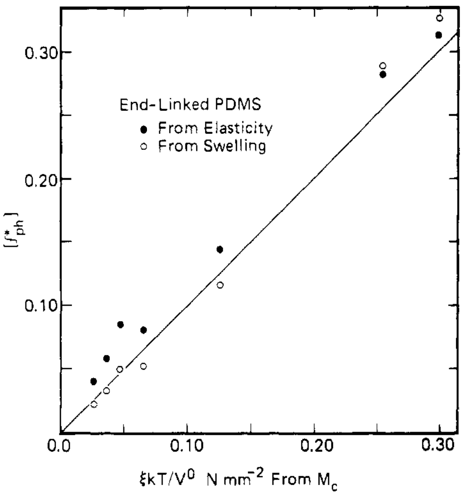

Figure 6. Limiting values of the reduced force, $[f^*_{ph}]$, deduced according to Figure 4 from the results of Mark and Sullivan[15] for end-linked PDMS networks plotted against $\xi kT/V^0$ from the molecular weights of the chains. Results from elasticity measurements are shown by filled circles and those from equilibrium swelling in benzene by open circles. The two highest points were obtained in like manner from elasticity measurements not included in Figure 4.

Introducing the condition for equilibrium by equating to zero the sum of contributions to the chemical potential from mixing with diluent and from the elastic response of the network, one obtains

$$\ln (1 - \upsilon_2) + \upsilon_2 + \chi \upsilon_2{}^2 + (\bar{V}_1 \xi / N_A V^0) \lambda^{-1} [1 + K(\lambda^2)] = 0$$

where χ is the familiar interaction parameter, $\bar{V}_1$ is the molar volume of the diluent, $\lambda = \upsilon_2{}^{-1/3}$ measures the linear dilation, and $K(\lambda^2)$ is defined by eq 37 of the preceding paper.[1] Substitution for ξ / V^0 according to eq 3 yields

$$[f^*_{ph}] = -(RT/\bar{V}_1)[\ln (1 - \upsilon_2) + \upsilon_2 + \chi \upsilon_2{}^2] \lambda / [1 + K(\lambda^2)] \quad (9)$$

The activities of benzene in swollen PDMS networks reported by Flory and Tatara[11] yield values of χ at 25 °C that can be approximated satisfactorily by

$$\chi = 0.48 + 0.35 \upsilon_2 \quad (10)$$

over the range in volume fraction υ_2 of interest here. This relationship is supported by the results of Shih and Flory[20] obtained from activities of benzene in mixtures with linear PDMS. From the swelling data of Mark and Sullivan,[15] treated according to eq 9 with χ given by eq 10 and $K(\lambda^2)$ calculated from eq 37 of the preceding paper using the values of κ quoted in Figure 4, we obtain the results shown by the open circles in Figure 6. They are well represented by the 45° line.

The foregoing calculations are very sensitive to the value of χ. The principal consequence of a small error in χ would be manifested in a change of the slope of the relationship portrayed by the open circles in Figure 6; the intercept, negligibly small, would be little affected. These results argue compellingly, therefore, against an intercept of significant magnitude that could be attributed to a contribution from trapped entanglements. The consistently higher values of $[f^*_{ph}]$ derived from elasticity measurements, shown by the filled circles in Figure 6, may reflect small departures from equilibrium in the force measurements.[15] Such departures are expected to be most pronounced for networks of low degrees of cross-linking in which the approach to equilibrium is protracted. The disparity between the two sets of data is small, irrespective of its source.

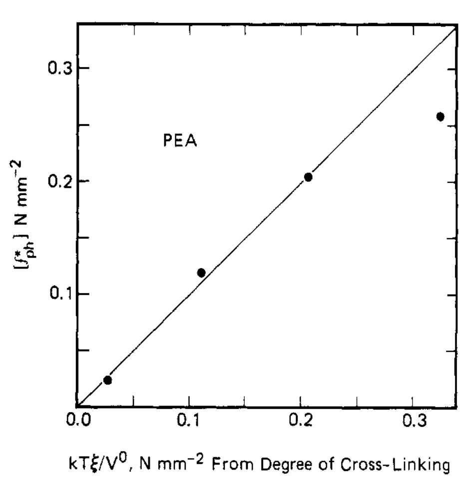

Figure 7. Limiting values of the reduced force for PEA networks, deduced from the analysis of data in Figure 5, plotted against $\xi kT/V^0$ from the chemically established degrees of cross-linking.

The intercepts for PEA networks, taken from Figure 5 and Table I, are plotted in Figure 7 against values of $\xi kT/V^0$ from the "chemical" degree of cross-linking. The points are well represented by the 45° line. There is no indication of a perceptible intercept.

Gottlieb et al.[21] have reached the opposite conclusion from their interpretation of a comprehensive array of data, gathered from 12 different sources, on networks of poly(dimethylsiloxane). They assert that discrete entanglements (i.e., "trapped entanglements" or "topological interferences" in their terminology) contribute substantially to the stress. Closer inspection reveals that the source of this discordance resides principally in two fundamental differences in the evaluation and analysis of experimental data. First, Gottlieb et al.[21] confine attention to stresses at small strains and they do not deduct the contribution to the reduced stress from restraints on junction fluctuations, this contribution being largest at small strains. Instead, they assume such fluctuations to be totally suppressed at small strains, as if $\kappa = \infty$ for all networks. More importantly, they treat this contribution as a constant fraction of the reduced stress for all degrees of cross-linking, contrary to our analysis and the supporting results examined above. Second, most of the measurements included by Gottlieb et al. in their survey were not conducted under conditions that ensure attainment of elastic equilibrium, especially in networks of low degrees of cross-linking. Measurements on swollen samples, which would have circumvented this difficulty, were not carried out.[22]

Both of these departures from our procedure and the underlying theory contribute divergences which enhance the reduced forces by factors that increase with decrease in the degree of cross-linking. Together, they conspire to yield a substantial intercept in the extrapolation of the reduced force to $\xi = 0$. This intercept is largely, if not entirely, a fiction of their analysis. It does not betoken a major contribution to the stress from topological entanglements. Their further assertion that our results on PEA support a substantial intercept is false.

Concluding Remarks

Our deductions showing that the reduced force $[f^*_{ph}]$, from which effects of diffuse entanglements have been removed, does not retain an appreciable contribution from discrete entanglements are reinforced by evidence reviewed elsewhere.[24,25] Discrete entanglements that engage one chain inextricably with another in the manner traditionally envisaged (see ref 26 and 27, for example) evidently are rare, or, if present, they do not enhance the effective degree of interlinking significantly. Inasmuch as this finding is at variance with views that are widespread on the intertwining of polymer chains in amorphous, condensed phases of polymers, it is appropriate to examine the basis and origin of these views.

Random configurations for real polymer chains generated by Monte Carlo procedures offer a clue. They do not lace back and forth as if guided by their time-averaged, mean destinations, as customary sketches of their trajectories imply.[26,27] The course of a given (instantaneous) configuration seldom oscillates in a manner that would engender entanglements through the winding of one chain about another. The misrepresentations of conventional diagrams in this respect may be rooted in common misconceptions on random walks and games of chance in general. They are not self-correcting in the sense that a large excursion in one direction presages correction by an opposite trend. Rigorous pronouncements of the theory of probability on this subject have been elegantly presented by Feller.[28]

The indicated equivalence of $[f^*_{\mathrm{ph}}]$ obtained from elasticity or swelling measurements to $\xi kT/V^0$ from chemical determinations allows one of the three parameters used in the analysis of experimental data to be removed from the category of quantities whose values may be arbitrarily assigned. Of the two remaining parameters, κ and ξ, values of the former for a series of networks from the same polymer appear to be related, through their degrees of cross-linking, according to eq 8. It is possible that κ can be obtained independently from the characteristic ratio of the given polymer through use of this equation if, in due course, the quantity denoted by I would be established as a universal parameter. In any case, κ appears to be subject to substantial restrictions. Choice in the values assigned to the remaining parameter ζ is quite arbitrary at the present level of theory and in the light of existing experimental evidence. Its role is minor compared to $[f^*_{\mathrm{ph}}]$ and κ.

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References and Notes

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