substituted instead of its partial specific volume, the refractive index increment of the complex becomes $\nu_\mu^* \doteq 0.816/(1 + 4.72 \times 1.03) = 0.14$, which is a reasonable value, in the first approximation proportional to the difference of the refractive indices of the complex and of the surroundings. The tabulated ν_μ are extremely high, because the measured difference of the refractive indices, Δn, is related to a considerably lower concentration of the polymer alone and not to that of the complex.

The application of systems possessing extremely high refractive index increments to light-scattering measurements with polymers of low molecular weight will be reported later. Preliminary measurements indicate that some complications can arise; these may be due to various causes, such as, e.g., the dependence of γ and ν_μ on molecular weight, changes in solvent composition in the space between the individual macromolecules induced by the addition of even a small amount of the polymer, or the not negligible changes in the intensity of light scattered from the solvent system with the variation of temperature common in measurements with a standard temperature control.

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Effect of Diluent on the Stress–Strain Isotherms and Ultimate Properties of a Crystallizable Polymer Network[1]

D. S. Chiu, T.-K. Su, and J. E. Mark*[2]

Department of Chemistry and the Macromolecular Research Center,
The University of Michigan, Ann Arbor, Michigan 48109.

Received April 15, 1977

ABSTRACT: The crystallizable networks investigated consisted of *cis*-1,4-polybutadiene chains cross-linked by means of a peroxide cure, a conventional sulfur cure, and γ radiation. The networks were studied in elongation to their rupture points, at 25 and 10 °C, both in the undiluted state and swollen with a nonvolatile diluent. (Values of the volume fraction v_2 of polymer in the networks were 1.00, 0.80, 0.60, 0.40, and 0.20.) The linear portions of the resulting isotherms were represented in terms of the equation $[f^*] = 2C_1 + 2C_2\alpha^{-1}$, where $[f^*]$ is the modulus or reduced stress, α is the relative length of the sample, and $2C_1$ and $2C_2$ are constants independent of α. The constant $2C_2$, which is a measure of the extent to which an actual isotherm departs from the form predicted by the simplest molecular theories, is found to decrease markedly with decrease in v_2, but approximates zero only in the limit of infinite swelling ($v_2 \rightarrow 0$). The constant $2C_1$ is independent of dilution to within experimental error, a result which supports the use of this component of $[f^*]$ in the calculation of network cross-link densities. Strain-induced crystallization, as evidenced by departures from this simple linearity at high elongations, was observed to decrease markedly with decrease in v_2. The changes observed do not support the existence of significant contributions to $[f^*]$ from "limited chain extensibility". When crystallites do form at high elongation, they would be expected to act simultaneously as physical cross-links and reinforcing filler particles. This was confirmed by the observation that suppression of strain-induced crystallization by increase in the amount of diluent present significantly decreased both the ultimate strength and elongation to break the networks. The fractional decrease in these quantities is much larger than it is in the case of noncrystallizable networks of poly(dimethylsiloxane).

One of the most important properties of a deformable polymer network is its resistance to rupture, as characterized by its ultimate strength and maximum extensibility. These two "ultimate properties" are much enhanced in the case of networks which can undergo strain-induced crystallization,[3,4] since the crystallites thus formed have a strong reinforcing effect within the network structure.[3,5] This crystallization would be expected to be diminished by swelling the network with diluent ("plasticizer"), which decreases the melting point T_m of the system.[3] An extremely important experiment is, therefore, the quantitative determination of the extent to which dilution diminishes the stress and elongation exhibited by a network at its rupture point. The most useful interpretation of such data would involve comparison of the fractional decrease in these quantities in the case of a crystallizable polymer network, with the corresponding decreases observed for a network known to be immune to strain-induced crystallization.[6-13] The crystallizable polymer chosen for the present investigation was *cis*-1,4-polybutadiene (*cis*-PBD). A previous study[7] of the ultimate properties of networks of this polymer in the unswollen state clearly demonstrated that it very readily undergoes strain-induced crystallization, as was shown earlier for networks of natural rubber[6,13] and synthetic *cis*-1,4-polyisoprene.[6] The required stress–strain isotherms for these same networks[7] were therefore determined, in elongation, at various degrees of dilution or network swelling. Corresponding results for a noncrystallizable network are already available, from a study[8] of the ultimate properties of unswollen and swollen networks of poly(dimethylsiloxane) (PDMS) at 30 °C, at a temperature sufficiently high in the case of this polymer to suppress entirely any strain-induced crystallization.[8,9]

The detailed shape of the isotherms just prior to rupture is also of considerable importance, particularly with regard to attempts[10,11] to interpret anomalous properties of networks at high elongation in terms of the "limited extensibility" of network chains. Specifically, if the marked increase or upturn in the network modulus $[f^*]$ which is frequently observed at high elongation were due to the limited extensibility of the network chains, then the upturn should persist at all dilutions, and an increase in swelling should decrease the elongation at which it becomes discernable.[12,13] On the other hand, if the upturn disappears with increase in swelling, this result would add to the already strong evidence[5,7–9] indicating that the anomalous increase in $[f^*]$ at high elongation is due to strain-induced crystallization.

These experiments also serve to establish the effect of swelling on the stress–strain isotherms in the region where $[f^*]$ shows a simple linear dependence on reciprocal elongation α^{-1}.[11,14] (As usual,[15–17] $[f^*]$ is defined as $fv_2^{1/3}/A^*(\alpha - \alpha^{-2})$, where f is the elastic force, v_2 is the volume fraction of polymer in the network, A^* is the unswollen undeformed cross-sectional area of the sample, and $\alpha = L/L_i$ is the length of the sample relative to its unstretched length in the swollen state). More specifically, values of the constants $2C_1$ and $2C_2$ in the semiempirical equation[18]

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

are determined with an unusually high degree of reliability since experiments carried out to the rupture point cover the widest possible range in the elongation α. It is obviously important to characterize the effect of swelling on these constants, in particular $2C_2$, which is widely used[11,14] as a measure of the extent to which an observed isotherm departs from the form predicted by the simplest molecular theories of rubberlike elasticity.[3,11] There is now a very plausible molecular explanation[19–22] of this long-puzzling contribution to $[f^*]$, and prediction of the dependence of $2C_2$ on swelling is one important question to which these new theories are being addressed.[21,22] An understanding of $2C_2$ is of course essential in gauging the validity of using experimental values of the constant $2C_1$ in the calculation of network cross-link densities.[14] For these reasons, it is important to determine, as reliably as possible, values of $2C_2$ and $2C_1$ for networks studied over as wide a range of elongation and swelling as is practicable.

Experimental Section

The *cis*-PBD samples were obtained from the same cross-linked sheets,[23] prepared and extracted as described previously.[7] There were a total of seven samples, which had been cross-linked using benzoyl peroxide (P1, P2), sulfur vulcanization (S1, S2), and γ radiation (G1–G3). The conditions used in their preparation are summarized in the second column of Table I. (Included for purposes of comparison in the lower portion of the table are results obtained at 30 °C for noncrystallizable networks of PDMS.)[8] Values of the cross-link density $\nu/2V$ at 25 °C and the average molecular weight M_c between cross-links[20,21,24] were calculated from the values of $2C_1$ previously determined for these networks in elongation in the unswollen state.[7,8] The relationship employed was

$$2C_1 = C\nu kT/V = C\rho kT/M_c \tag{2}$$

in which the constant C was assigned the value $\frac{1}{2}$, on the basis of the most recent and most reliable theoretical[20–22] and experimental studies.[24] These results are given in columns three and four. (The PDMS networks were intentionally of relatively low degree of cross-linking. This was necessary in order to obtain the desired high extensibility, since these networks could not benefit from reinforcing effects resulting from strain-induced crystallization.)[9]

The temperature chosen for the investigation of networks P1 and P2 was 25 °C, since this temperature was known to be sufficiently low for strain-induced crystallization in these two samples.[7] Temperatures of 25 and/or 10 °C were employed for the other five networks. The diluent employed at 25 °C was 1,2,4-trichlorobenzene ($T_m \simeq 17$ °C); the lower melting diluent 1,2-dichlorobenzene ($T_m \simeq -17$ °C) was used for the measurements at 10 °C. The values of v_2 chosen for this study were 1.00, 0.80, 0.60, 0.40, and 0.20, with the degree of swelling being adjusted to the extent that each actual value of v_2 deviated from its specified value by less than ±0.01.

A number of test strips were cut from each of the sample sheets. The stress–strain isotherm for each strip was then measured in the usual manner,[7,8] using a series of increasing elongations until the point of rupture was reached. (Thus, a different test strip had to be used for each value of v_2 investigated.) More often than not, rupture occurred in the vicinity of the clamped regions. Several tests for reversibility, the results of which are described below, were carried out on one strip from sample G3 swollen to the highest degree of dilution ($v_2 = 0.20$).

Results and Discussion

The stress–strain data were represented using plots of $[f^*]$ against reciprocal elongation α^{-1}, as suggested by eq 1, with values of the elongation at rupture being shown by small vertical arrows placed along the abscissa. The isotherms thus obtained for samples P1 and P2 at 25 °C are shown in Figures 1 and 2, respectively. Those obtained for samples S1 and S2 at 25 °C were found to be linear within experimental error for all values of v_2, and these samples were therefore also studied at 10 °C. Although results for both temperatures are tabulated and discussed below, only the isotherms at 10 °C are shown, in Figures 3 and 4, respectively. The isotherms for samples G1–G3 were obtained at 10 °C, and these are presented in Figures 5–7.

The reversibility tests conducted on sample G3 at $v_2 = 0.20$ gave results similar to those obtained earlier on unswollen *cis*-PBD networks.[7] Measurements restricted to the linear portion of the isotherm were highly reproducible, but once the elongation became sufficiently large to induce crystallization, as evidenced by departures from linearity, the data in the linear region were no longer exactly reproduced upon decrease in elongation. Reproducibility was restored, however, by returning the sample to the undeformed state, thereby melting the network crystallites, and then remeasuring the isotherm using a series of increasing elongations. These results are important since they indicate that little if any chain scission was occurring prior to rupture.

The linear portion shown for each stress–strain isotherm was located by least-squares analysis. Values of the slope of each line, $2C_2$ in eq 1, are given in column seven of Table I. Since the quantity of primary interest here is the fractional decrease in $2C_2$ with increase in dilution or swelling (decrease in v_2), each value of $2C_2(v_2)$ for a particular network was divided by the value $2C_2(1.0)$ obtained for that network in the unswollen state. All of the results obtained, for PDMS[8] as well as *cis*-PBD, are shown in Figure 8. The point corresponding to $v_2 = 1.0$ may be artificially high, because of nonequilibrium contributions to $2C_2$ in the case of a network in the unswollen state.[14] It was therefore ignored in the least-squares analysis of these data, the result of which is the line shown through the remaining points. The constant $2C_2$ is seen to decrease with decrease in v_2, as has long been known to be the case.[11,14,25] From this analysis, however, it appears that $2C_2$ approximates zero only in the limit of infinite dilution ($v_2 \rightarrow 0$), as was concluded earlier in a more limited study,[16] of PDMS networks.

The values of $2C_1$, also obtained from the linear portions of the isotherms, are given in the final column of Table I. In order to show the effect of dilution on this constant, which is known to be relatively independent of v_2,[11,14,25] each of these values was also normalized using the value $2C_1(1.0)$ obtained for that particular network in the unswollen state. The results are shown in Figure 9, in which the ordinate has been greatly expanded, to the extent that the entire range shown corresponds to a change of only ±10% in $2C_1(v_2)/2C_1(1.0)$. The scatter in these results seems to increase with decrease in v_2, presumably because of difficulties in conducting elasticity measurements on very highly swollen networks. In any case, the average deviation of this ratio from unity is only a few percent, which is less than the experimental uncertainty in measurements of this type. In fact, the least-squares line shown suggests that over the entire range $v_2 = 1.0$–0.20, $2C_1$ is constant to within only a few tenths of a percent. These

Table I
Sample Characteristics and Values of the Mooney-Rivlin Constants

Sample[a]	Cross-linking conditions	$10^5\nu/2V$,[b] mol cm^{-3}	$10^{-3}M_c$,[b] g mol^{-1}	T, °C	v_2	$2C_2$, N mm^{-2}	$2C_1$, N mm^{-2}
P1	Peroxide, 1%, 120 °C, 1 h	6.06	7.50	25	1.00	0.0864	0.142
					0.80	0.0382	0.140
					0.60	0.0215	0.138
					0.40	0.0121	0.138
					0.20	0.0091	0.135
P2	Peroxide, 1%, 120 °C, 6 h	6.94	6.50	25	1.00	0.0366	0.172
					0.80	0.0286	0.167
					0.60	0.0167	0.169
					0.40	0.0104	0.169
					0.20	0.0049	0.168
S1	Sulfur, 1%, 150 °C, 2 h	7.66	5.90	25	1.00	0.203	0.203
					0.80	0.141	0.202
					0.60	0.100	0.202
					0.40	0.0763	0.196
					0.20	0.0501	0.204
				10	1.00	0.283	0.173
					0.80	0.203	0.171
					0.60	0.138	0.175
					0.40	0.0776	0.173
					0.20	0.0314	0.181
S2	Sulfur, 2%, 150 °C, 1 h	8.84	5.15	25	1.00	0.270	0.246
					0.80	0.209	0.248
					0.60	0.170	0.250
					0.40	0.127	0.259
					0.20	0.103	0.266
				10	1.00	0.315	0.197
					0.80	0.231	0.200
					0.60	0.166	0.204
					0.40	0.114	0.206
					0.20	0.0822	0.208
G1	γ radiation, 11.2 Mrad	3.94	11.5	10	1.00	0.190	0.0904
					0.80	0.123	0.0868
					0.60	0.0752	0.0915
					0.40	0.0417	0.0933
					0.20	0.0288	0.0878
G2	γ radiation, 15.9 Mrad	6.00	7.55	10	1.00	0.204	0.150
					0.80	0.156	0.147
					0.60	0.116	0.143
					0.40	0.0550	0.151
					0.20	0.0359	0.147
G3	γ radiation, 19.7 Mrad	6.96	6.50	10	1.00	0.240	0.166
					0.80	0.180	0.166
					0.60	0.117	0.168
					0.40	0.0759	0.164
					0.20	0.0396	0.165
PDMS-3	γ radiation, 0.63 Mrad	0.480	100.6	30	1.00	0.0246	0.0118
					0.80	0.0134	0.0121
					0.60	0.0113	0.0117
					0.40	0.0042	0.0126
PDMS-2	γ radiation, 0.77 Mrad	0.857	56.4	30	1.00	0.0315	0.0218
					0.80	0.0145	0.0220
					0.60	0.0106	0.0218
					0.40	0.0082	0.0208
PDMS-1	γ radiation, 0.90 Mrad	1.20	40.3	30	1.00	0.0267	0.0304
					0.80	0.0178	0.0298
					0.60	0.0134	0.0299
					0.40	0.0093	0.0305

[a] The P, S, and G samples are *cis*-PBD; the PDMS samples are poly(dimethylsiloxane),[8] which is noncrystallizable under the conditions employed in its study. [b] Calculated using $2C_1 = \nu kT/2V = \rho kT/2M_c$.[7,20,21,24]

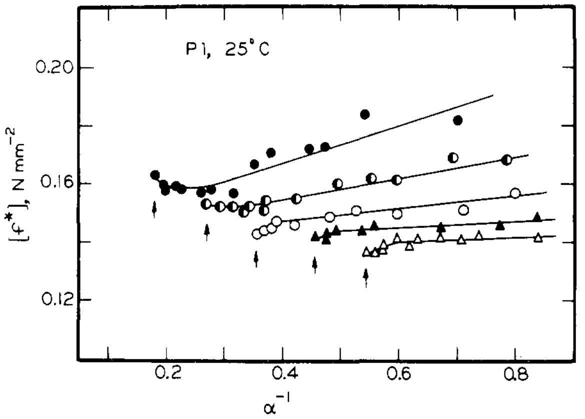

Figure 1. Stress-strain isotherms for *cis*-1,4-polybutadiene network P1, cross-linked to a relatively low degree by means of benzoyl peroxide, and studied in both the unswollen and swollen states. The following information pertains to both this figure and the following six figures for the other *cis*-PBD networks. Values chosen for the volume fraction v_2 of polymer in each network were 1.00 (●), 0.80 (◐), 0.60 (○), 0.40 (▲), and 0.20 (△); the diluent employed at 25 °C was 1,2,4-trichlorobenzene, and at 10 °C it was 1,2-dichlorobenzene. The arrows locate the values of the elongation α at which rupture occurred.

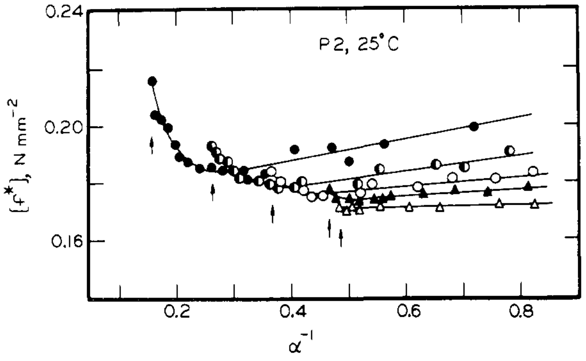

Figure 2. Stress-strain isotherms for peroxide-cured network P2, which has a somewhat higher degree of cross-linking than P1.

results thus strongly support the wide-spread use of the $2C_1$ component of $[f^*]$ in the calculations of network cross-link densities.

The nonlinear portions of the stress-strain isotherms vary considerably from one type of sample to another. This may be due to changes in the stereochemical structure of the chains occurring during some of the cross-linking procedures,[26] or to different chain length distributions in the resulting networks. As is well known,[7,27,28] a decrease or "downturn" in $[f^*]$ is due to the high spatial extension of the network chains along the axis of deformation as they form axially oriented crystallites. A subsequent increase or "upturn" in $[f^*]$ was then attributed primarily to the simultaneous functioning of these crystallites as cross-links within the network structure. The value of the elongation α_d at the downturn, when it occurred, was gotten from each of the isotherms. These values were then adjusted for the effect of swelling prior to the uniaxial stretching by the factor $v_2^{-1/3}$. The resulting values of the total elongation $\lambda_d = \alpha_d v_2^{-1/3}$ at the downturn in $[f^*]$ are given in the fourth column of Table II. The effect of cross-link density on λ_d is shown by the results obtained on G1–G3. Increase in $\nu/2V$ is seen to decrease the elongation at which $[f^*]$ turns downward; this is consistent with the reasonable expectation that short network chains become sufficiently oriented for strain-induced crystallization at smaller elongations than do longer network chains.[9] The most interesting result, however, is the finding that λ_d generally *decreases* with increase in

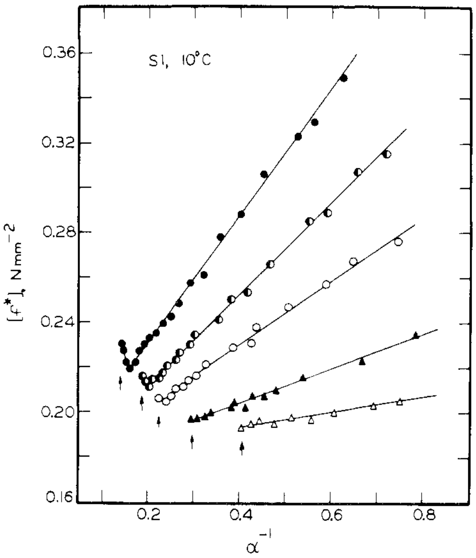

Figure 3. Stress-strain isotherms for sulfur-cured network S1, of moderate degree of cross-linking, at 10 °C.

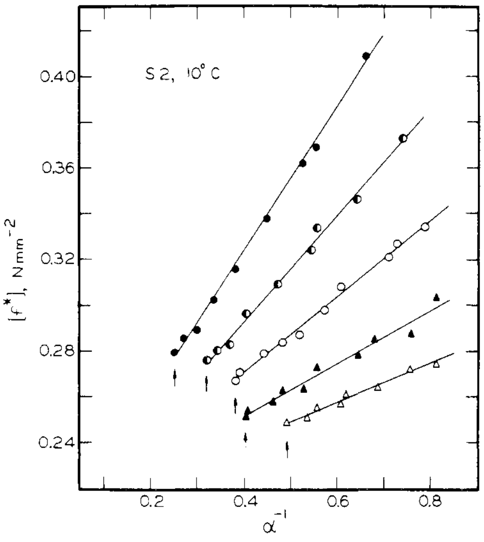

Figure 4. Stress-strain isotherms for sulfur-cured network S2, of relatively high degree of cross-linking, at 10 °C.

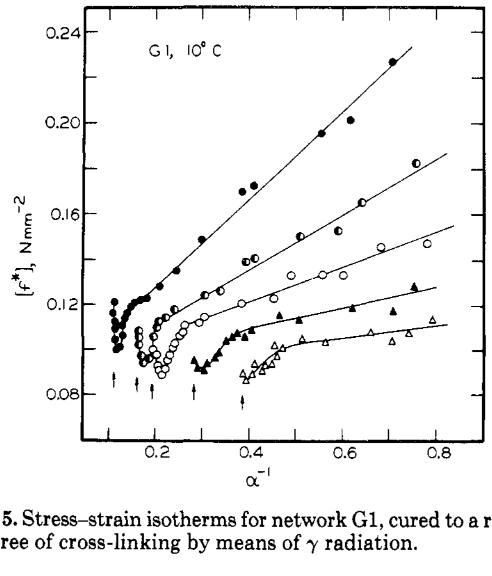

Figure 5. Stress-strain isotherms for network G1, cured to a relatively low degree of cross-linking by means of γ radiation.

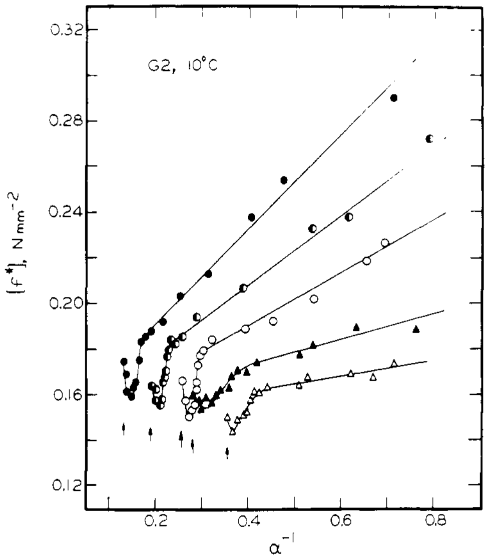

Figure 6. Stress–strain isotherms for network G2, cured to a moderate degree of cross-linking by means of γ radiation.

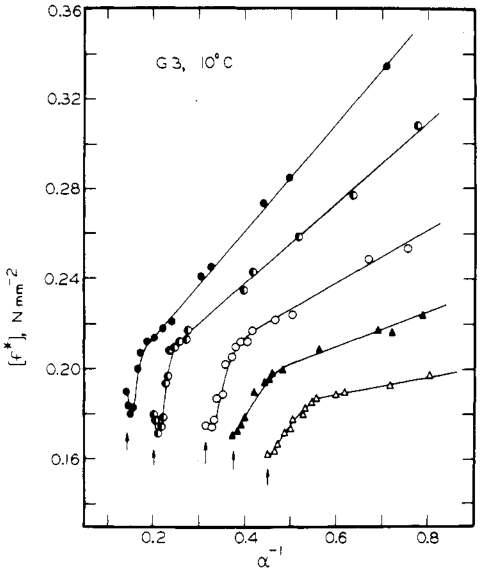

Figure 7. Stress–strain isotherms for network G3 cured to a relatively high degree of cross-linking by means of γ radiation.

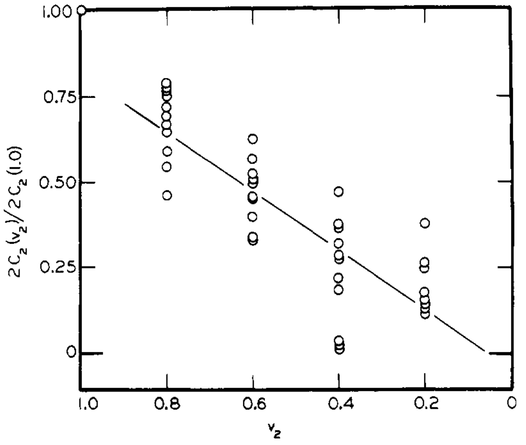

Figure 8. Values of the Mooney-Rivlin constant $2C_2$ (expressed relative to values in the unswollen state) shown as a function of the volume fraction of polymer in the network.

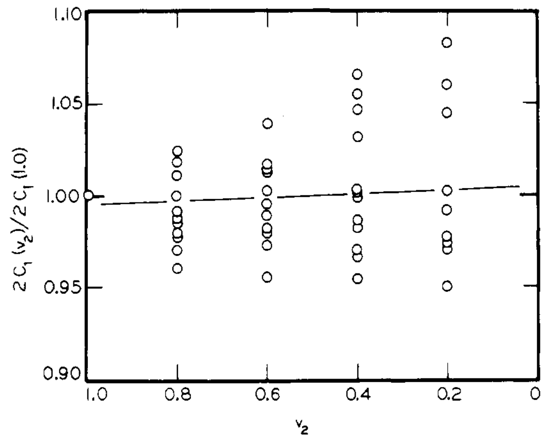

Figure 9. Values of the Mooney-Rivlin constant $2C_1$ (expressed relative to values in the unswollen state) shown as a function of the volume fraction of polymer in the network.

swelling. This suggests that depression of the melting point of the network chains due to the presence of diluent is less important, at least in these networks, than is the increase in the rate of crystallization due to the relatively high chain mobility in a swollen network. Also of interest is the observation that strain-induced crystallization can readily occur in a network swollen to a value of v_2 as low as 0.20.

The elongation α_u at the upturn in $[f^*]$ was also obtained from Figures 1–7, and values of $\lambda_u = \alpha_u v_2^{-1/3}$ are given in the fifth column of Table II. As expected, the decrease in λ_u with increase in $\nu/2V$ parallels the decrease shown by λ_d. Similarly, λ_u was found to decrease with decrease in v_2. The *magnitude* of the increase in $[f^*]$ is seen to decrease with swelling, indicating that although swelling facilitates the first appearance of strain-induced crystallization, it clearly diminishes the total amount of crystallinity attainable. Most importantly, this increase in $[f^*]$ generally disappears entirely at the highest dilutions. These results are of course difficult to reconcile with suggestions that limited chain extensibility is the origin of the upturn in $[f^*]$ at high elongations.

Values of the total elongation at rupture $\lambda_r = \alpha_r v_2^{-1/3}$ are given for all of the samples in column six of Table II. Decrease in temperature from 25 to 10 °C in the case of samples S1 and S2 is seen to increase λ_r, through increase in the amount of strain-induced crystallization. Increase in degree of cross-linking decreases λ_r as a direct result of the shortening of the network chains. Similarly, increase in swelling decreases λ_r, and very markedly, as would be expected from decrease in the total amount of crystallinity, as described above. The ratio $\lambda_r(v_2)/\lambda_r(1.0)$ represents the fractional decrease in the total elongation to rupture due to network swelling. Values of this quantity for all of the samples are given in column seven of Table II. The results for two typical *cis*-PBD samples P1 and G1 are shown in Figure 10; included for purposes of comparison are the corresponding results for the first of the PDMS samples. The fractional decrease in λ_r is much larger for the *cis*-PBD samples, because of the already mentioned decrease in the strain-induced crystallization accompanying the swelling of the network. Specifically, for change in v_2 from 1.0 to 0.20, the decrease is approximately 50% for P1 and G1, and only 20% for PDMS-1.

The ultimate strength of a polymer network is probably best represented by the nominal stress $f^* \equiv f/A^*$ at rupture. Values of this quantity for all of the networks are given in column eight of Table II. As expected from the previous discussion, f_r^* is decreased by either an increase in temperature or increase in swelling. Similarly, the fractional quantity $f_r^*(v_2)/f_r^*(1.0)$ decreases with decrease in v_2 much more markedly

Table II
Characteristics of the Nonlinear Portions of the Isotherms and the Ultimate Properties of the Networks

Sample	T, °C	v_2	λ_d[a]	λ_u[b]	λ_r[c]	$\lambda_r(v_2)/\lambda_r(1.0)$	f_r^*,[d] N mm^{-2}	$f_r^*(v_2)/f_r^*(1.0)$
P1	25	1.00		3.85	5.50	1.000	0.891	1.000
		0.80		3.31	4.02	0.731	0.598	0.671
		0.60	3.08		3.34	0.607	0.455	0.511
		0.40	2.80		2.96	0.538	0.379	0.425
		0.20	2.95		3.16	0.575	0.363	0.407
P2	25	1.00		3.57	6.33	1.000	1.36	1.000
		0.80		2.91	4.10	0.648	0.772	0.567
		0.60		2.70	3.24	0.512	0.560	0.411
		0.40		2.74	2.91	0.460	0.461	0.338
		0.20			3.53	0.558	0.534	0.392
S1	25	1.00			4.95	1.000	1.19	1.000
		0.80			4.14	0.836	0.977	0.822
		0.60			3.94	0.796	0.884	0.744
		0.40			3.16	0.638	0.665	0.560
		0.20			3.32	0.671	0.658	0.554
	10	1.00		6.25	7.04	1.000	1.61	1.000
		0.80		5.52	5.73	0.814	1.22	0.763
		0.60		5.27	5.29	0.751	1.07	0.669
		0.40			4.61	0.655	0.886	0.552
		0.20			4.17	0.592	0.743	0.463
S2	25	1.00			2.56	1.000	0.831	1.000
		0.80			2.34	0.914	0.744	0.895
		0.60			2.33	0.910	0.679	0.817
		0.40			2.32	0.906	0.595	0.716
		0.20			2.69	1.050	0.662	0.797
	10	1.00			3.97	1.000	1.09	1.000
		0.80			3.36	0.846	0.897	0.823
		0.60			3.11	0.783	0.778	0.714
		0.40			3.34	0.841	0.787	0.722
		0.20			3.49	0.879	0.762	0.699
G1	10	1.00	7.41	8.00	8.70	1.000	1.05	1.000
		0.80	5.52	5.98	6.53	0.751	0.706	0.672
		0.60	4.65	5.51	6.08	0.700	0.599	0.570
		0.40	3.62	4.52	4.76	0.547	0.444	0.423
		0.20	3.53		4.38	0.503	0.370	0.352
G2	10	1.00	6.06	6.90	7.46	1.000	1.30	1.000
		0.80	4.79	5.13	5.61	0.752	0.909	0.702
		0.60	4.09	4.31	4.62	0.619	0.752	0.581
		0.40	3.48	4.38	4.85	0.649	0.758	0.585
		0.20	4.07	4.62	4.81	0.644	0.685	0.529
G3	10	1.00	5.88	6.45	6.99	1.000	1.32	1.000
		0.80	4.49	5.13	5.31	0.760	0.943	0.712
		0.60	3.12	3.65	3.77	0.540	0.639	0.483
		0.40	2.89		3.62	0.518	0.584	0.441
		0.20	3.17		3.79	0.542	0.559	0.422
PDMS-3	30	1.00			6.14	1.000	0.0958	1.000
		0.80			6.05	0.985	0.0884	0.923
		0.60			5.73	0.933	0.0795	0.830
		0.40			5.49	0.894	0.0748	0.781
PDMS-2	30	1.00			5.59	1.000	0.151	1.000
		0.80			5.20	0.930	0.130	0.855
		0.60			5.37	0.961	0.128	0.848
		0.40			4.76	0.852	0.107	0.706
PDMS-1	30	1.00			4.90	1.000	0.176	1.000
		0.80			4.42	0.902	0.149	0.846
		0.60			4.12	0.841	0.136	0.771
		0.40			4.16	0.849	0.135	0.768

[a] Total elongation at the downturn in $[f^*]$. [b] Total elongation at the upturn in $[f^*]$. [c] Total elongation at rupture. [d] The nominal stress f/A^* at rupture.

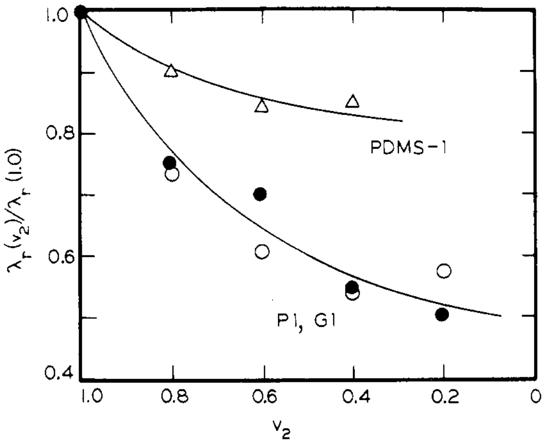

Figure 10. The effect of dilution on the total elongation at rupture (expressed relative to values obtained in the unswollen state) for two typical *cis*-PBD networks, P1 and G1. Included for purposes of comparison in this and the final figure are analogous results obtained for a typical noncrystallizable network of poly(dimethylsiloxane).[8]

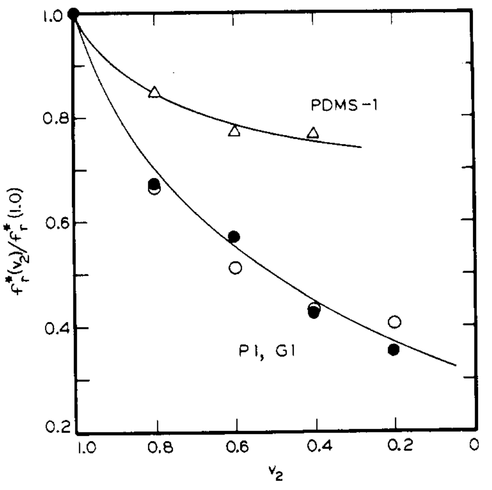

Figure 11. The effect of dilution on the ultimate strength (expressed relative to values obtained in the unswollen state).

for the *cis*-PBD samples than for the PDMS samples, as is shown by the entries in the final column. Figure 11 shows these results for the same networks used for purposes of illustration in Figure 10. For decrease in v_2 from 1.0 to 0.20, this ratio decreases approximately 65% for the *cis*-PBD networks and only 30% for the PDMS network.

The above effects of strain-induced crystallization on the ultimate properties of a polymer network pertain to experiments in which efforts are made to bring the system as closely as possible to elastic equilibrium. Also of importance would be comparisons between the ultimate properties of crystallizable and noncrystallizable networks determined in continuous extension as a function of rate of deformation.

Acknowledgments. It is a pleasure to acknowledge, with gratitude, the financial support provided by the National Science Foundation through Grant DMR 76-20036 (Polymers Program, Division of Materials Research). D. S. Chiu and T.-K. Su also wish to thank the Macromolecular Research Center of the University of Michigan for postdoctoral fellowships.

References and Notes

(1) Presented in part before the Rubber Division of the American Chemical Society, Chicago, 1977. It is a pleasure to dedicate this paper to Dr. Maurice L. Huggins on the occasion of his 80th birthday.
(2) Author to whom correspondence should be addressed at the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221.
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(4) Such crystallization arising from the stretching of a polymer network is frequently referred to in the literature as "stress-induced" crystallization. We feel that this is a misnomer, since the more relevant quantity is the *strain*. A network under a large uniform hydrostatic stress, for example, would not show the pronounced crystallization readily occurring in the same network upon elongation at a much lower level of stress.
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