TABLE I
NETWORK PARAMETERS FOR ANIONICALLY PREPARED POLYSTYRENE GELS, OBTAINED FROM SWELLING, UNILATERAL COMPRESSION, AND SWELLING PRESSURE MEASUREMENTS

Sample no.	M_c	q_c	q	$10^5 q_0^{-2/3}\nu^*$	χ	β	$\langle r^2\rangle_c/\langle r^2\rangle_0$
1823	18,700	6.7	10.3	0.82	0.51	0.5	0.45
1822	9,400	6.8	6.8		0.53	0.5	
1889	17,400	7.7	10.9	0.71	0.53	0.5	0.45
1865	10,400	7.7	8.2				
1819	10,000	10.6	≈11	0.96			0.45
1887	14,000	11.1	12.4	0.69	0.53	0.5	0.45
1860	10,100	11.1	≈10	1.14			0.55
1818	7,200	11.1	9.2	1.66	0.53	0.4	0.55
1888	17,600	15.4	17.9	0.42	0.52	0.5	0.45
1864	10,400	15.4	11.8				

0.525 ± 0.005 over the range $6 \leq q \leq 18$. Its value is higher than in more dilute polystyrene solutions in benzene, a finding similar to that reported in toluene by Dušek[6] for networks prepared by radical copolymerization of styrene and DVB. Although no detailed molecular explanation of the higher values for the semiempirical χ parameter can be given, the presence of DVB cross-links could be held responsible for these results.

The "memory" parameter $q_0^{-2/3}$ is related to the volume fraction of polymer prior to cross-linking, q_c^{-1}, as follows[2]

$$q_0^{-2/3} = q_c^{-2/3}\langle r^2\rangle_c/\langle r^2\rangle_0$$

when $\langle r^2\rangle_c$ and $\langle r^2\rangle_0$ stand for the mean-square end-to-end dimensions of the chains after cross-linking and in the unstrained reference state, respectively. Without any assumption, therefore, our data yield

$$\frac{q_0^{-2/3}\nu^* q_c^{-2/3}}{B\nu^*} = \frac{\langle r^2\rangle_c/\langle r^2\rangle_0}{B} = 1.0 \pm 0.2 \qquad (5)$$

Frequently the assumption that the chain dimensions do not change upon cross-linking is made. In that case our results would indicate that $B = 1$. Such a conclusion has in the past been considered implausible by Dušek[7] and more recently also by Mark,[1,8] because it would mean that upon cross-linking at q_c no syneresis would ever occur, regardless of how many cross-links are introduced. It has, however, been pointed out previously[2] that the χ parameter may very well increase as a result of cross-linking, thus leading to a gel of lower diluent compatibility at higher degrees of cross-linking, resulting in syneresis. Moreover, the assumption that $\langle r^2\rangle_c = \langle r^2\rangle_0$ is not necessarily valid.

Further analysis requires an assumption about ν^*. If our networks are not inhomogeneously cross-linked and if no network defects of any type exist, ν^* equals ρ_p/M_c. Inserting this, we find for all our gels, without any assumption about $\langle r^2\rangle_c$ and $\langle r^2\rangle_0$

$$B = 0.5 \pm 0.1 \qquad (6)$$

This is an interesting result because the gels vary widely in cross-linking conditions (ν^*, q_c). If network defects were to play an important role, one would also expect B to vary widely for the various gels. One is therefore tempted to conclude that the DVB-living polystyrene solutions indeed form uniform networks with DVB nodules and no dangling DVB blocks. Accepting this, the Flory–Wall identification, $B = 2/f$, then leads to an average functionality of a DVB cross-link of 4, which is quite reasonable.

Continuing this more speculative part of our analysis, we would then also conclude from eq 5 that (see Table I)

$$\langle r^2\rangle_c/\langle r^2\rangle_0 = 0.5 \pm 0.1 \qquad (7)$$

This result would indicate that upon cross-linking all gels exhibit a uniform shrinkage by a factor of 2.0 ± 0.2 in the mean-square end-to-end dimensions of the chains. A trend in this direction has recently been derived by Chompff,[9] whereas a much older estimate of James and Guth[10] comes up with exactly this factor of 2.

It should be emphasized that the results embodied in eq 6 and 7 are based on a somewhat uncertain assumption about ν^*. Thus the major conclusion of this paper, that the Flory–Wall theoretical value of B is the correct one, is not absolutely unassailable. On different grounds, the same can be said of the analogous conclusion of Johnson and Mark. Insertion of eq 7 into their data, however, still leaves the Flory–Wall value as the strongest contender. It seems unlikely that further time and effort invested in this problem utilizing other networks and experimental methods will succeed in removing any remaining vestige of doubt.

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[8] J. E. Mark, *J. Amer. Chem. Soc.*, **92**, 7252 (1970).

(9) A. J. Chompff in "Polymer Networks, Structure and Mechanical Properties," A. J. Chompff and S. Newman, Ed., Plenum Press, New York, N. Y., 1971, p 463 ff.

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Compression Behavior of Natural Rubber Vulcanized in the Swollen State

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The Gaussian theory for rubberlike network elasticity gives the following expression for the stress[1]

$$\tau = nKT\frac{\langle r^2\rangle_d}{\langle r^2\rangle_0}(\alpha - \alpha^{-2}) \qquad (1)$$

where τ is the force on the unit of unstrained cross-sectional area, n is the number of elastic chains in the volume unit, K is the Boltzmann constant, T is the absolute temperature, $\langle r^2\rangle_d$ and $\langle r^2\rangle_0$ are the mean-square end to end distances respectively for a network chain and a free chain, and α is the strain ratio.

Equation 1 is valid for dry rubber; for swollen systems, we have

$$\tau_d = nKT\frac{\langle r^2\rangle_d}{\langle r^2\rangle_0}V_S^{-1/3}(\alpha - \alpha^{-2}) \qquad (1a)$$

where τ_d is the stress per unit of dry unstrained cross section, $n\langle r^2\rangle_d/\langle r^2\rangle_0$ refers to the dry network, and V_S is the volume fraction of polymer. Equations 1 and 1a are valid for monodirectional forces both in extension and in compression. It is well known, however, that the experimental data do not agree with eq 1 and 1a and that the stress–strain isotherms are

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(1) P. J. Flory, *J. Amer. Chem. Soc.*, **78**, 5222 (1956).

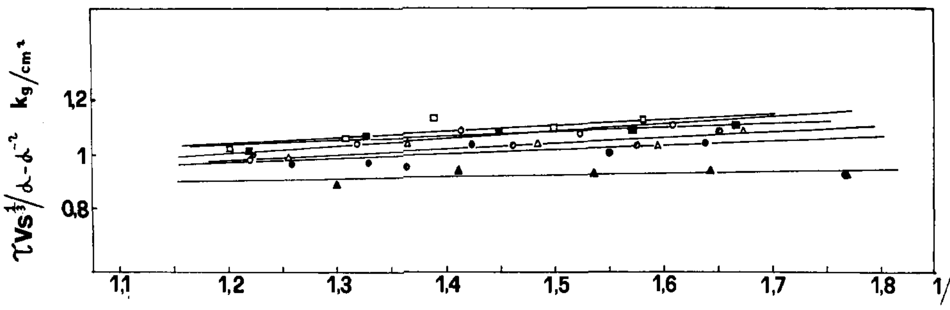

Figure 1. Mooney–Rivlin plots obtained in compression on sample N.R.C.: (●) $V_S = 1$, (○) $V_S = 0.898$, (□) $V_S = 0.811$, (■) $V_S = 0.737$, (◐) $V_S = 0.664$, (△) $V_S = 0.616$, (▲) $V_S = 0.556$. N.R.C. in extension gives $2C_1 = 0.97$ and $2C_2 = 0.32$ kg/cm².

better described by the phenomenological Mooney–Rivlin equation[2]

$$\tau = 2C_1(\alpha - \alpha^{-2}) + 2C_2(1 - \alpha^{-3}) \qquad (2)$$

It is of theoretical interest to find some correlation between eq 1 and 2 and to discuss in molecular terms the two coefficients C_1 and C_2. Information in this direction can be obtained by analyzing the elastic behavior of swollen networks both in extension and in compression. In previous works[3,4] it has been shown that conventional vulcanizates have in compression an elastic modulus variable with the swelling and that such a variability seems to be correlated with the swelling behavior of the $2C_2$ coefficient given by extension measurements. On the other hand it has been observed that natural rubber, vulcanized in the swollen state, obeys eq 1 in extension.[5] In other words, the vulcanizates in the swollen state can behave as an ideal rubber, giving a C_2 coefficient equal to zero and a C_1 coefficient invariable with the swelling.[5] In the present work we have analyzed the compression behavior of such vulcanizates in order to test their ideality under different strain conditions.

Experimental Section

The stress–strain isotherms were obtained as previous described,[3] with 15-min intervals between different points. The temperature was 30° in all cases. Decalin was used as a swelling solvent, and for the swollen samples the stress τ_d was corrected with the coefficient $V_S^{1/3}$. Results have been treated with eq 2, plotting $\tau_d \cdot V_S^{1/3}/(\alpha - \alpha^{-2})$ *vs.* $1/\alpha$. No change in swelling degree was observed during deformation. Straight lines were obtained by least squares. The samples were prepared as previously described,[5] using decalin as a solvent for the vulcanization mixture. Three different samples of natural rubber, indicated as N.R.A., N.R.B., and N.R.C. with different amounts of solvent, were examined. Indicating by ϕ_r the rubber fraction in the vulcanization mixture, we have: $\phi_r = 0.25, 0.30$, and 0.35 for N.R.A., N.R.B., and N.R.C., respectively. Dicumyl peroxide was used as a vulcanization initiator, using 3% of the polymer weight.

Results and Discussion

In Table I, results are reported in terms of $\tau_d V_S^{1/3}/(\alpha - \alpha^{-2})$ $(1/\alpha = 1.3)$ *vs.* the swelling degree V_S. The Mooney–Rivlin plots obtained with sample N.R.C are reported in Figure 1. For N.R.C, the stress–strain isotherms give in extension $2C_1 = 0.97$ kg/cm² and $2C_2 = 0.32$ kg/cm². The data of Table I and Figure 1 underline clearly three fundamental points: the coefficient $2C_2$ is nearly zero, the modulus does not change with the swelling, and compression and ex-

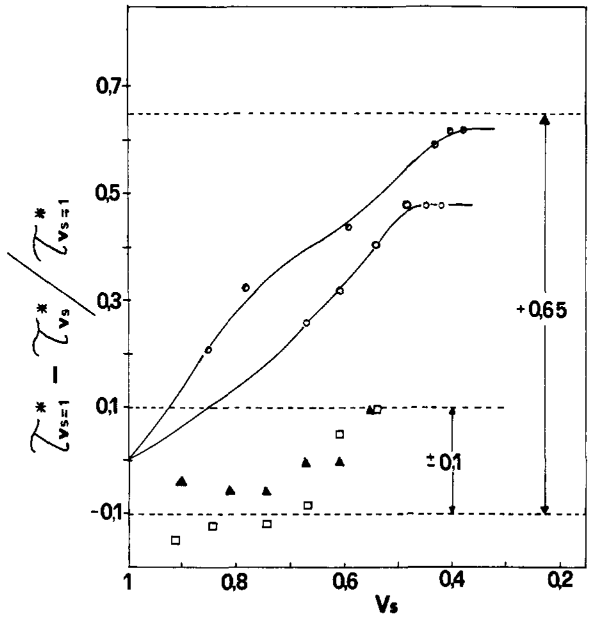

Figure 2. $(\tau^*_{V_S=1} - \tau^*_{V_S})/\tau^*_{V_S=1}$ *vs.* V_S, where $\tau^*_{V_S} = \tau_d V_S^{1/3}/\alpha - \alpha^{-2}$ $(1/\alpha = 1.3)$: (▲) N.R.C, (□) N.R.B, (○, ●) conventional vulcanizates with different amounts of vulcanization initiator.

TABLE I

V_S	$\tau_d V_S^{1/3}/(\alpha - \alpha^{-2})^a$
N.R.A., $\phi_r = 0.25$	
1	0.66
0.851	0.58
0.726	0.65
0.625	0.55
0.514	0.52
N.R.B., $\phi_r = 0.30$	
1	0.98
0.916	1.15
0.837	1.14
0.739	1.12
0.668	0.92
0.615	1.06
N.R.C., $\phi_r = 0.35$	
1	1.00
0.898	1.04
0.811	1.05
0.737	1.06
0.664	1.00
0.616	1.00
0.556	0.92

[a] τ_d is reported in kilograms per square centimeter. $1/\alpha = 1.3$.

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[2] L. R. G. Treolar, "The Physics of Rubber Elasticity," 2nd ed, Oxford University Press, 1958.

[3] F. de Candia and A. Ciferri, *Makromol. Chem.*, **134**, 335 (1970).

[4] F. de Candia and L. Amelino, *J. Polym. Sci., Part A-2*, in press.

[5] C. Price, G. Allen, F. de Candia, M. C. Kirkham, and A. Sumbramaniam, *Polymer*, **11**, 486 (1970).

tension measurements give the same modulus. At the same time, we can observe that there is a direct relationship between the value of C_2 in extension and the value of the elastic modulus in compression. As a matter of fact, a zero value for C_2 in extension[6] gives in compression an elastic modulus invariable with the swelling, as is shown in Table I and Figure 1; on the other hand, in the conventional vulcanizates a decrease of C_2 with swelling in extension takes place with a strong decrease of the compression modulus.[3,4] In Figure 2 the relative modulus decreases are reported for two conventional vulcanizates and two of our vulcanizates. As shown, for conventional networks the decrease is of the order of 50–60%, while for solution vulcanizates the values are in the range ±10%.

The results demonstrate, therefore, that natural rubber vulcanized in the swollen state behaves as an ideal network, obeying eq 1. In this case, the C_1 coefficient of the Mooney–Rivlin equation in compression can be identified with the theoretical modulus of eq 1. It is independent of the strain conditions, extension or compression, and of the swelling degree.

Many suggestions can be made to interpret this result. First of all, according to what we have previously reported,[5] it is possible to say that our vulcanizates have a low percentage of physical entanglements in comparison with a conventional vulcanizate. A second hypothesis regards the last works of Prins,[7–9] in which the nonideality of the rubber networks is correlated with a certain degree of supramolecular organization in the amorphous material (bundles). As a matter of fact, vulcanization "stops" the topology of the polymer at the moment in which it takes place, and in our case it stops the topology of a polymer diluted by the solvent. Solvent removal allows an approach of the cross-link points, with a consequent supercoiling of the network chains. It is less probable, therefore, that parallel segments of adjacent chains can interact with bundle formation, owing to the supercoiled state of the network chains. Experimental studies are now in progress to verify this latter hypothesis.

(6) This result has been previously reported.[5]

(7) R. Blokland and W. Prins, *J. Polym. Sci., Part A-2*, **7**, 1595 (1969).

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

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Communications to the Editor

An Audiofrequency Resonance in the Quasielastic Light Scattering of Polymer Gels

We have observed a broad resonance in the frequency spectrum of the light scattered quasielastically by two dilute polymer gels. The resonance occurs at a few kilohertz and has been traced to underdamped, oscillatory behavior of viscoelastic, microscopic heterogeneities in the structural makeup of the gels.

Figure 1 shows the frequency distribution of the scattered light of a 1% aqueous solution of agarose (an alternating copolymer of 3,6-anhydro-α-L-galactopyranose and β-D-galactopyranose) at 70° as well as that of the gel obtained by cooling the solution to a temperature below the gel point at 42°. Figure 2 shows the results for a 5% poly(vinyl alcohol) gel in a mixture of water and ethylene glycol obtained by quenching the solution from 80 to 5° and subsequently measuring at room temperature. In this case, the maximum disappears upon aging of the gel.

The measurements were performed in a homodyning light-scattering spectrometer[1] consisting basically of a He–Ne laser (Spectraphysics Model 124), a thermostated rectangular glass cell of 2-mm optical path, and a wave analyzer (General Radio Model 1800 A) connected to a photomultiplier with a 10- or 33-K load resistor. The wave analyzer output was squared and accumulated in the memory of a multichannel analyzer (Technical Measurements, CAT 1000) for about 10 min, representing about eight sweeps through a preselected, motor-driven frequency range. The squaring assures that the power spectrum of the photocurrent is stored in the memory of the multichannel analyzer.[2] By utilizing an arbitrary static scatterer in the position of the sample cell, it was ascertained that the response to shot noise was flat over the entire frequency range covered in our measurements.

The rectangular sample cell and its thermostated jacket allowed measurements to be taken at external scattering angles, θ_e, varying from 10 to 50°. By inserting a Polaroid in the scattered beam, it was established that the frequency-shifted scattering was not depolarized. The same was true for the integrated Rayleigh scattering of the gels which was measured in an absolute light-scattering photometer without a homodyning arrangement. We are thus dealing with isotropic, quasielastic scattering, for which we can write the Rayleigh ratio, $R(\mathbf{K}, \omega)$, as follows

$$R(\mathbf{K}, \omega) = (16\pi^4/\lambda_0^4)\langle\eta^2\rangle \int_V d\mathbf{r} \int_{-\infty}^{+\infty} \gamma(\mathbf{r}, \tau)e^{i\mathbf{K}\mathbf{r}}e^{-i\omega\tau}d\tau \qquad (1)$$

Here λ_0 is the wavelength of the incident radiation *in vacuo* (λ_0 632.8 nm); $\langle\eta^2\rangle$ is the mean-square polarizability fluctuation of a volume element, characterized by a time–space correlation function $\gamma(\mathbf{r}, \tau)$, defined in such a way that $\gamma(\mathbf{r}, \tau) = \gamma(\mathbf{r}, -\tau)$; $\mathbf{K}$ is the scattering vector[2,3] which equals $(4\pi/\lambda)\cdot\sin\theta/2$, where λ is the wavelength and θ the scattering angle in the sample; and ω is the circular frequency *minus* that of the incident radiation. Upon performing the integration over the scattering volume, V, the power spectrum of the scattered light will be given by

$$R(\mathbf{K}, \omega) = (16\pi^4/\lambda_0^4)\langle\eta^2\rangle \int_{-\infty}^{+\infty} \Gamma(\mathbf{K}, \tau)e^{-i\omega\tau}d\tau \qquad (2)$$

where $\Gamma(\mathbf{K}, \tau) = \Gamma(\mathbf{K}, -\tau)$ is a time-correlation function.

The homodyning spectrometer measures the power spectrum of the photocurrent autocorrelation $\langle i(t)i(t+\tau)\rangle$. Since $i(t)$ is proportional to the scattered light intensity, *i.e.*, to the square of the scattered field, the power spectrum of the photocurrent, $S_i(\mathbf{K}, \omega)$, is proportional to the Fourier transform of the square of $\Gamma(\mathbf{K}, \tau)$[1]

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