

Molecular Mobility in Swollen Cross-linked Rubbers. Viscoelasticity and Diffusion Measurements

Chiu-Ping WONG,* John L. SCHRAG, and John D. FERRY

*Department of Chemistry and Rheology Research Center, University
of Wisconsin, Madison, Wisconsin, 53706, U.S.A.*

(Received December 21, 1970)

ABSTRACT: Creep and low-frequency dynamic viscoelastic measurements in shear have been made on two series of lightly cross-linked natural rubber samples swollen to different extents in nonvolatile solvents. The time and frequency regions corresponded to the zone of slow, secondary relaxation mechanisms in such networks. The diffusion of radioactively tagged *n*-hexadecane in trace amounts through these samples has also been measured, reflecting local molecular mobility. Viscoelastic data at different temperatures were combined by the method of reduced variables in the usual manner. Data at different degrees of swelling (measured by the polymer volume fraction, v_2) could be approximately superposed by reduced variables with the frequency scale shifted by a factor λ_2 and the compliance magnitude scale multiplied by a factor \mathfrak{A} . The factor λ_2 decreased with decreasing v_2 much more rapidly than the ratio of diffusion constants, D_0/D , in the dry and swollen rubbers; the ratio $\lambda_2/(D_0/D)$ was approximately $v_2^{3.5}$. The factor \mathfrak{A} was proportional to a power of v_2 intermediate between the values of 1/3 expected for a Gaussian cross-linked network and 2 expected for an entanglement network; this power decreased with increasing cross-link density. The data were compared with previous results on cross-linked rubbers diluted *before* cross-linking, and on swollen networks of poly(β -hydroxyethyl methacrylate).

KEY WORDS Cross-link / Rubber / Swelling / Slow Relaxations /
Trace Diffusion / Long-Range Mobility /

The effect of added diluents of low molecular weight on molecular mobility of amorphous uncross-linked polymers has been widely investigated.¹ Short-range mobility can be gauged either by viscoelastic measurements in the transition zone or by diffusion of small foreign molecules; the effect of diluent in increasing mobility (decreasing local frictional resistance) appears to be equivalent in the two experiments^{2,3} and closely related to free volume.²⁻⁷ Long-range mobility in polymers of high molecular weight is governed by local friction plus entanglement coupling;⁸ it is gauged by viscoelastic measurements in the plateau and terminal zones. The portion of the concentration dependence of the terminal relaxation time which is attributable to entanglement changes can be separated, for example, by comparing the effects of diluent in the transition and terminal zones.^{8,9}

* Present address: Mellon Institute, Pittsburgh, Pennsylvania, 15213, U.S.A.

In a diluted lightly cross-linked network, the concentration dependence of local mobility can be expected to be much the same as in an uncross-linked polymer, whether the diluent is introduced before or after cross-linking, since the local motions will be largely oblivious of the cross-links. But long-range motions must be considered quite differently.^{10,11} The origin of slow relaxation mechanisms is not even certain, although it has been attributed to entanglement of dangling branched structures partially attached to the cross-linked network.^{12,13} The concentration dependence of the equilibrium modulus or compliance depends on whether the diluent is introduced before or after cross-linking,¹⁴⁻¹⁷ and the magnitudes of time or frequency dependent compliances vary with concentration in a complicated manner.¹⁸

In the present work, the concentration dependence of slow relaxation mechanisms has been studied by viscoelastic measurements on

two series of rubber networks swollen to various degrees after cross-linking, and compared with some earlier measurements on rubbers with cross-links introduced in the presence of diluent.¹⁹ Previously published data on diffusion of small molecules in these diluted rubbers,^{4,19} together with some additional new data, permit identification of the portion of the concentration dependence of the relaxation times attributable to long-range topological features. The concentration dependence of the magnitudes of compliance associated with these slow relaxation mechanisms is also examined.

EXPERIMENTAL

Materials

The cross-linked rubbers used in these experiments were generously prepared for us by Drs.

P. Thirion and R. Chasset, Institut Français du Caoutchouc, Paris. Natural rubber specially selected for high purity was cross-linked with dicumyl peroxide. Details are given in previous publications,^{19,20} where the same code numbers are used. Series 128 was cross-linked in the presence of diluent (ASTM oil No. 3) as previously described.¹⁹ For the series B₂-40, the diluent (1,1-diphenylethane) was introduced after cross-linking by swelling in the presence of benzene which was later removed.⁴ For the series B₁-20, the diluent (Primol D, a naphthenic oil²¹) was introduced after cross-linking in a similar manner. (A control sample was also swollen with benzene and dried without introduction of oil; a weight loss of 0.4% was incurred.) Characteristic data on the dry and swollen samples are summarized in Table I. The equilibrium compliance (units cm²/dyne) is

Table I. Characterization of cross-linked natural rubbers

Rubber code	log J_e	Ref	v_2	Diluted ^a	ρ
B ₁ -20 ^b	-5.98	20	0.502	A	0.897
			0.632	A	0.901
			0.761	A	0.905
			1.000		0.913
B ₂ -40 ^c			0.536	A	0.951
			0.663	A	0.941
			0.772	A	0.932
			1.000		0.914
128-III ^d	-6.41	20	0.63	B	0.917
128-IV ^d	-6.35 ^e	19	0.63	B	0.918
128-V ^d	-6.44 ^e	19	0.63	B	0.918

^a A, after cross-linking; B, before cross-linking.

^b Initial molecular weight 260000; diluent Primol D.

^c Initial molecular weight 230000; diluent 1,1-diphenylethane.

^d Initial molecular weight 540000; diluent ASTM oil No. 3.

^e Refers to *dry* network, after extraction of diluent.

given as an index of the degree of cross-linking; v_2 is the volume fraction of rubber. The density, ρ , was measured pycnometrically for the 128 series and for the others was calculated on the basis of volume additivity.

The radioactively tagged *n*-hexadecane used in diffusion experiments with the B₁-20 series has been described elsewhere.²²

Diffusion Measurements

Measurements were made with the B₁-20 series by the thin smear method³ and the diffusion

coefficient D was calculated by matching with theoretical curves taking into account contributions to measured activity from below the sample surface.²² The temperature was between 24.92 and 25.00°C.

Viscoelastic Measurements

The Plazek torsion pendulum²³ was used to measure dynamic mechanical properties in free torsional oscillations in the frequency range from 0.06 to 3 Hz at temperatures from -8 to 45°C. The loss tangents ($\tan \delta$) and storage (J') and

loss (J'') compliances were calculated in the usual manner.²⁰ For the final calculations, a Univac 1108 computer was used; the program is reported elsewhere.²⁴ For the B₂-40 series, shear creep measurements were also made over times up to 34 hr at about 24°C.

RESULTS

Diffusion Measurements

Values of $\log D$ for the B₁-20 series with Primol D as diluent and hexadecane as penetrant are listed in Table II. The other diffusion data

Table II. Diffusion coefficients of hexadecane in B₂-20 series swollen in Primol D

v_2	$\log D$ (cm ² sec ⁻¹)
0.492	-6.862
0.633	-6.946
0.755	-7.016
0.996	-7.134 ^a
1.000	-7.138 ^b

^a Untreated dry rubber; v_2 listed reflects the 0.4% weight loss in preparing the sample below.

^b Swollen with benzene and dried for consistency with treatment of the other samples.

to be quoted in the discussion section have already been published.^{4,19} The increase in diffusion coefficient with dilution is considerably less than observed previously with 1,1-diphenylethane as diluent, presumably because the Primol D introduces less additional fractional free volume.

Viscoelastic Measurements

The creep measurements on the three swollen samples of the B₂-40 series at 24°C are shown in Figure 1, together with the creep of the corresponding dry rubber measured by Dickie^{20,25} at 25.2°C; the creep compliance $J(t)$ is plotted

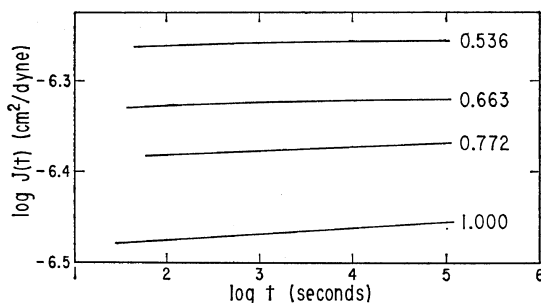


Figure 1. Creep compliance plotted logarithmically against time for dry rubber B₂-40 and three samples swollen in 1,1-diphenyl ethane. Numbers give volume fraction of polymer.

logarithmically against time. The small temperature difference is not significant. Individual points are not shown but will appear in the concentration reduction of these data below. With increasing dilution, the magnitude of $J(t)$ increases and the slope diminishes.

Dynamic measurements were made on the B₂-40 series, for each sample at 6 different temperatures followed by a check run at 25°C. Numerical data are reported elsewhere.²⁴ The data were reduced to 25°C by shift factors a_T determined empirically and then fitted to an equation of the WLF form:

$$\log a_T = -c_1(T-298)/(c_2+T-298) \quad (1)$$

The coefficients c_1 and c_2 are listed in Table III, but no particular significance is attached to their values because of the limited temperature range covered. The storage compliance J' , with magnitudes reduced to $T_0=298^\circ\text{K}$ by the factor $T\rho/T_0\rho_0$ (where ρ and ρ_0 are the densities at T and T_0), is plotted logarithmically against ωa_T in Figure 2 together with the loss tangent $\tan \delta = J''/J'$. Curves for the dry rubber^{20,25} are included without points. With increasing dilu-

Table III. WLF parameters for swollen rubbers

Rubber code	v_2	Temperature range	c_1	c_2
B ₁ -20	0.502	-6 to 44°C	5.67	206
	0.632	-5 to 45°C	5.18	176
	0.761	-5 to 45°C	4.06	131
B ₂ -40	0.536	-8 to 44°C	3.6	135
	0.663	-6 to 45°C	2.7	103
	0.772	-6 to 44°C	2.47	93
128 (all)	0.63	-5 to 45°C	2.16	80

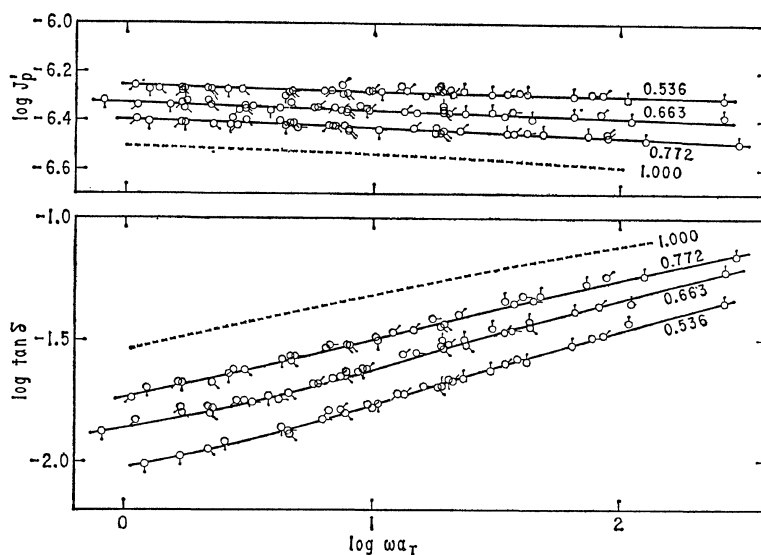


Figure 2. Storage compliance and loss tangent plotted logarithmically against radian frequency after reduction to 25°C, for the same samples of Figure 1, identified by volume fraction of polymer. Key to approximate temperatures of measurement: pip up, -5°; successive 45° rotations clockwise are 5, 15, 25, 35, and 45°C.

tion, the magnitude of J' increases while the dispersion of $\tan \delta$ shifts to higher frequencies.

Similar dynamic results were obtained for the B₁-20 series; the data will be shown below after concentration reduction. The WLF parameters,

as well as those for the 128 series previously published, are included in Table III. All the numerical data are tabulated elsewhere.²⁴

Concentration Reduction of Viscoelastic Data

The description of concentration dependence

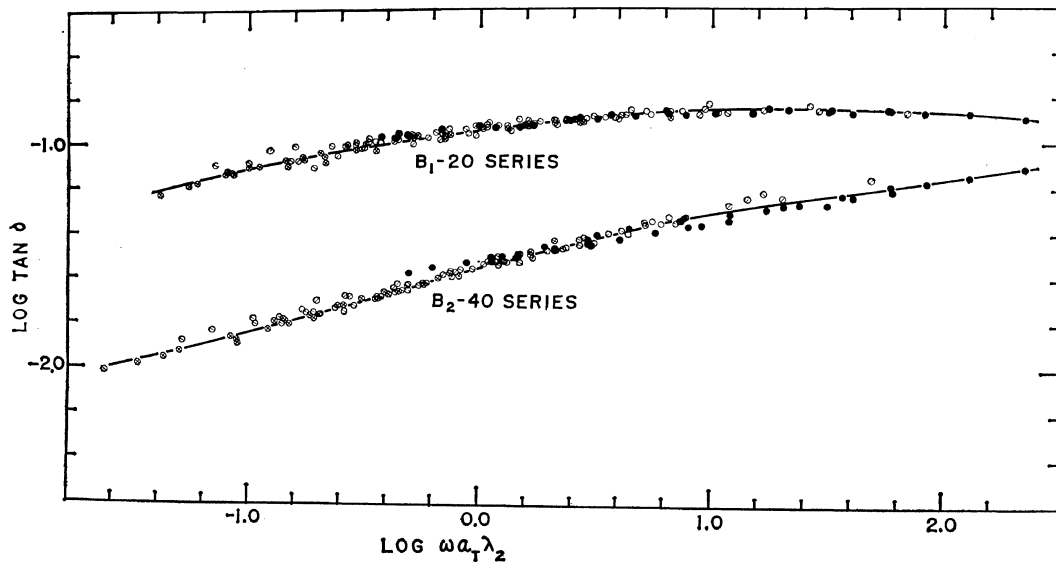


Figure 3. Loss tangent plotted logarithmically against $\omega a_T \lambda_2$, for the B₂-40 series of Figure 2 and the corresponding B₁-20 series. Concentration key: polymer volume fractions (*cf.* Table I) in increasing order are ⊗, ⊙, ∅, and ● (dry rubber).

by reduced variables must be approached with caution, especially in swollen networks.¹⁸ The frequency and time scales of Figures 1 and 2 correspond to the slow secondary relaxation mechanisms which have been studied extensively in lightly cross-linked rubbers.^{10,11,13,20,26} From analysis of stress relaxation measurements on several types of rubber (natural, styrene-butadiene, and *cis*-polybutadiene), Thirion and Chasset have shown that reduced variables can be applied in this range with arbitrary shifts in

time scale and magnitude of modulus.^{10,11} This implies that the long relaxation times associated with these mechanisms all have the same concentration dependence specified by a shift factor λ_2 (this notation by analogy with the treatment of concentration dependence in the terminal zone for uncross-linked polymers^{8,9}). It follows that, for dynamic measurements, values of $\tan \delta$ in this region should superpose when plotted against $\omega\lambda_2$; the effect of concentration on the magnitudes of the compliances does not enter here

Table IV. Concentration reduction parameters

Rubber	ν_2	$\log \lambda_2$	$\log \mathfrak{A}$	$\log D_0/D$		$\log \lambda_2 \nu_2^{-3.5}$
				HXD ^a	DPE ^b	
B ₁ -20	0.502	-1.30	-0.31	-0.27		-0.25
	0.632	-0.80	-0.23	-0.19		-0.10
	0.761	-0.55	-0.115	-0.12		-0.13
B ₂ -40	0.536	-1.71	-0.20	-0.74	-0.83	-0.77
	0.663	-1.20	-0.14	-0.58	-0.64	-0.58
	0.772	-0.79	-0.085	-0.42	-0.46	-0.40
128-III	0.63	-1.1	-0.25	-0.37		-0.4
128-IV	0.63	-1.1	-0.18	-0.38		-0.4
128-V	0.63	-1.1	-0.16	-0.40		-0.4

^a Hexadecane.

^b 1,1-diphenylethane.

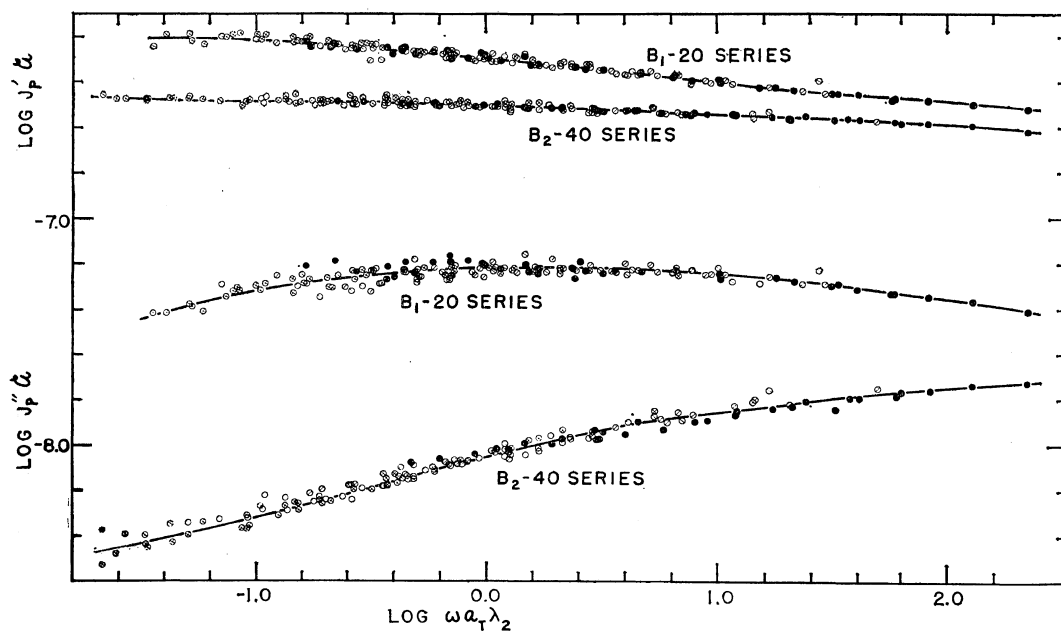


Figure 4. Storage and loss compliances, multiplied by the magnitude reduction factor \mathfrak{A} and plotted logarithmically against $\omega a_1 \lambda_2$, for the B₂-40 and B₁-20 series. Concentration key same as in Figure 3.

since $\tan \delta$ is a dimensionless ratio. In fact, very good superposition is obtained in this manner for both the B₂-40 and the B₁-20 series, as shown in Figure 3. The values of $\log \lambda_2$ chosen empirically for this plot, based on the dry rubber as the reference state, are listed in Table IV.

To superpose J' and J'' , a shift in magnitude is necessary as well as in the frequency scale. Whereas for uncross-linked polymers in the transition zone the appropriate factor appears to be v_2 , and in the plateau zone often v_2^2 , for swollen cross-linked networks it must be chosen empirically.¹⁸ Denoted by \mathfrak{A} as in previous studies of cross-linked polyhydroxyethyl metha-

crylate gels,¹⁸ this factor is also given in Table IV and is used to reduce the compliances by plotting $J'\mathfrak{A}$ and $J''\mathfrak{A}$ logarithmically against $\omega a_T \lambda_2$ for all temperatures and concentrations in Figure 4. Data for the dry rubbers ($\lambda_2 = \mathfrak{A} = 1$) are included in these plots; the reduction is very good. Also, the same factors can be used to reduce the creep data of Figure 1, as shown in Figure 5. The reduced creep data join smoothly with the reduced storage compliance; the slope is so small that $J'(t^{-1})$ is equal to $J(t)$ to a very close approximation.²⁷ A similar treatment for the previously published dynamic data of the 128 series is shown in Figure 6.

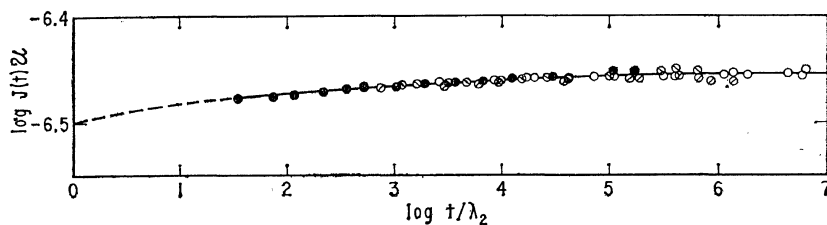


Figure 5. Creep compliance, multiplied by the magnitude reduction factor \mathfrak{A} and plotted logarithmically against time, for the B₂-40 series of Figure 1. Polymer volume fractions in increasing order are \circ , \square , \diamond , and \otimes . Dashed line at left is $J'(1/t)$ from Figure 4.

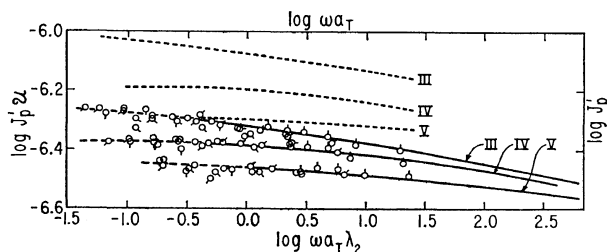


Figure 6. Storage compliance of swollen samples of 128 series, before (dotted lines, top and right scales) and after (tagged points, bottom and left scales) concentration reduction by the factors λ_2 and \mathfrak{A} . The solid curves drawn through the points are the data for the corresponding dry (extracted) rubbers. Approximate temperature key same as in Figure 2.

DISCUSSION

Concentration Dependence of Mobility and Relaxation Processes

The concentration dependence of relaxation processes involving motions of short segments can be described by a factor a_c , the ratio of the monomeric friction coefficient in the presence of diluent to its value in the undiluted polymer;²⁸

the viscoelastic relaxation times for processes in the transition zone differ by this factor, always < 1 . In one case this ratio is close to the ratio D_0/D of diffusion coefficients of a small molecule in the undiluted polymer and in the solution,³ and this equivalence will be assumed in the present analysis although it is somewhat uncertain for natural rubber.⁴

In the terminal zone of undiluted polymers of

high molecular weight, the viscoelastic relaxation times with and without diluent differ by a factor, λ_2 , which is the product of a_c and an additional structural factor associated with entanglement coupling. The concentration dependence of λ_2 is more marked than that of a_c ; in some cases $\lambda_2/a_c = v_2^{-2.4}$, as would be expected from certain treatments of entanglement coupling.¹

In the swollen cross-linked networks studied here, also, the concentration-dependent factor λ_2 changes much more rapidly with concentration than does D_0/D , as can be seen in Table IV. In Figure 7, $\log \lambda_2$ is plotted against v_2 , showing

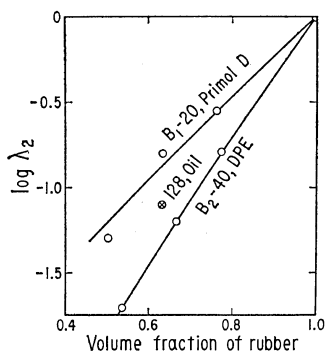


Figure 7. $\log \lambda_2$ plotted against v_2 ; series and diluents as indicated.

that the slow relaxation times are diminished by a factor of 50 when 46% of 1,1-diphenylethane is introduced. The differences among the different series can be attributed primarily to the effectiveness of the respective diluents on a_c (or D_0/D) through their fractional free volumes. An even stronger concentration dependence of λ_2 was observed by Thirion and Chasset in stress relaxation of rubbers swollen in ASTM oil No. 3.^{11,29}

If the additional structural factor in cross-linked networks were proportional to $v_2^{-2.4}$ as in uncross-linked polymers, D_0/D would be equal to $\lambda_2 v_2^{-2.4}$. Actually, it is found empirically to be approximately $\lambda_2 v_2^{-3.5}$, as shown in the last column of Table IV and in Figure 8. This exponent cannot be given a theoretical interpretation at present, but it seems reasonable that the effect of entangled structures in a network¹² should have a stronger concentration dependence than that of entanglements of linear molecules.

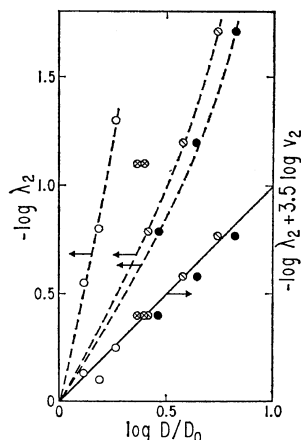


Figure 8. $\log \lambda_2$ (dashed curves) and $\log \lambda_2 v_2^{3.5}$ (solid line drawn with slope of 1) plotted against $\log D/D_0$. Hexadecane as penetrant: \circ , B₁-20 series; \otimes , B₂-40 series; \otimes , 128 series. 1,1-Diphenylethane as penetrant: \bullet , B₂-40 series.

Concentration Dependence of Magnitude of Compliance

The magnitude reduction factor \mathcal{U} is plotted logarithmically against v_2 for the B₁-20 and B₂-40 series in Figure 9. For an uncross-linked polymer

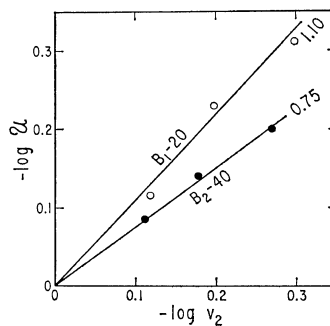


Figure 9. $\log \mathcal{U}$ plotted against $\log v_2$ for the B₁-20 and B₂-40 series. Slopes are indicated.

in the plateau zone, where the number of entanglement junctions can be expected to be proportional to v_2^2 unless specific loci of attraction are present, a slope of 2 would be anticipated; for a perfect cross-linked network, the equilibrium compliance should be proportional to $v_2^{-1/3}$ in accordance with the theory of rubberlike elasticity.³⁰ The observed slopes are intermediate between 1/3 and 2. A similar analysis for natural rubber, styrene-butadiene rubber,

and *cis*-polybutadiene swollen in ASTM oil No. 3 gives a slope near 2/3.²⁹

If the factor \mathcal{A} is empirically expressed as proportional to v_2^a , as in earlier studies of swollen networks of poly(β -hydroxyethyl methacrylate),¹⁸ the exponent a can be obtained also for the samples of series 128 although only one measurement at a single v_2 is available for each degree of cross-linking. In Figure 10, the exponent a is plotted against $\log G_e$ ($= -\log J_e$)

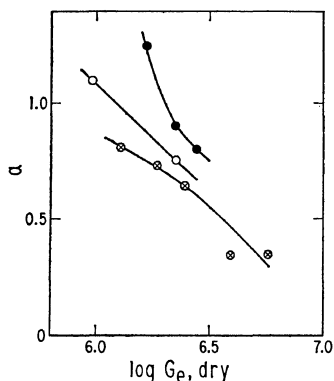


Figure 10. Exponent a plotted against equilibrium modulus. ○, Series B₁-20 and B₂-40; ●, Series 128; ⊗, poly(β -hydroxyethyl methacrylate), Series A of ref 18.

as a measure of cross-link density, for the following series: B₁-20 and B₂-40, from Figure 9; the 128 series; and Series A from ref 18, poly(β -hydroxyethyl methacrylate) networks swollen in diethylene glycol. Here G_e refers to the dry polymer. In each case the exponent diminishes with increasing cross-link density, corresponding to the qualitative expectation that the system becomes progressively less like an entanglement network and more like a network whose effective strands are terminated solely by permanent cross-links. The difference between the B₁-20—B₂-40 pair and the 128 series may be associated with the fact that the former were swollen after and the latter were diluted before the cross-links were introduced. Of course, an adequate description must be far more complicated than this; there must be contributions to the viscoelastic properties from both tangled and permanently cross-linked strands in varying proportions, and scrutiny of viscoelastic functions over wider ranges of frequency would probably reveal

changes in shape with concentration so that the concentration reduction illustrated in Figures 3—5 could not be achieved.

Moreover, studies with poly(β -hydroxyethyl methacrylate)¹⁸ showed that with still higher degrees of cross-linking the exponent a can become smaller than the 1/3 expected for a perfect Gaussian network and can even become negative. This behavior is attributed to severe extension of network strands at even moderate degrees of swelling so that Gaussian statistics no longer apply. Mechanical properties of such extended networks deserve further study.

Acknowledgments. This work was supported in part by a grant from the National Science Foundation. We are indebted to Mr. Barry A. Krieg for help with some of the calculations.

REFERENCES

1. J. D. Ferry, "Viscoelastic Properties of Polymers", 2nd ed., Wiley, New York, N.Y., 1970, Chapter 17.
2. J. R. Richards, K. Ninomiya, and J. D. Ferry, *J. Phys. Chem.*, **67**, 323 (1963).
3. R. S. Moore and J. D. Ferry, *J. Phys. Chem.*, **66**, 2699 (1962).
4. C. P. Wong, J. L. Schrag, and J. D. Ferry, *J. Polym. Sci., Part A-2*, **8**, 991 (1970).
5. H. Fujita, *Adv. Polym. Sci.*, **3**, 1 (1961).
6. R. E. Pattle, P. J. A. Smith, and R. W. Hill, *Trans. Faraday Soc.*, **63**, 2389 (1967).
7. R. A. Muir Martin, R. E. Pattle, and P. J. A. Smith, *Trans. Faraday Soc.*, **66**, 2340 (1970).
8. K. Ninomiya, J. R. Richards, and J. D. Ferry, *J. Phys. Chem.*, **67**, 327 (1963).
9. Y. Oyanagi and J. D. Ferry, *J. Colloid Sci.*, **21**, 547 (1966).
10. P. Thirion and R. Chasset, "Proceedings International Conference on Physics of Non-Crystalline Solids", North Holland Publishing Co., Amsterdam, 1965, p 345.
11. P. Thirion and R. Chasset, *J. Macromol. Sci.—Phys.*, in press.
12. N. R. Langley, *Macromolecules*, **1**, 348 (1968).
13. N. R. Langley and J. D. Ferry, *Macromolecules*, **1**, 353 (1968).
14. M. C. Shen and A. V. Tobolsky, *J. Polym. Sci., Part A*, **2**, 2513 (1964); *ibid.*, *Part A*, **3**, 629 (1965).
15. B. Meissner, I. Klier, and S. Kuchařik, *J. Polym. Sci., Part C*, **16**, 793 (1967).
16. C. Price, G. Allen, F. de Candia, M. C. Kirk-

- ham, and A. Subramaniam, *Polymer*, **11**, 486 (1970).
17. J. Hasa and M. Ilavský, *Collect. Czech. Chem. Commun.*, **34**, 2189 (1969).
 18. J. Janáček and J. D. Ferry, *J. Polym. Sci., Part A-2*, **7**, 1681 (1969).
 19. N. R. Langley, R. A. Dickie, C. P. Wong, J. D. Ferry, R. Chasset, and P. Thirion, *J. Polym. Sci., Part A-2*, **6**, 1371 (1968).
 20. R. A. Dickie and J. D. Ferry, *J. Phys. Chem.*, **70**, 2594 (1966).
 21. N. W. Tschoegl and J. D. Ferry, *Kolloid-Z. Z. Polym.*, **189**, 37 (1963).
 22. S. P. Chen and J. D. Ferry, *Macromolecules*, **1**, 270 (1968).
 23. D. J. Plazek, M. N. Vrancken, and J. W. Berge, *Trans. Soc. Rheol.*, **2**, 39 (1958).
 24. C. P. Wong, Ph. D. Thesis, University of Wisconsin, 1970.
 25. R. A. Dickie, Ph. D. Thesis, University of Wisconsin, 1965.
 26. R. Chasset and P. Thirion, *Rev. gen. Caoutchouc*, **44**, 1041 (1967).
 27. J. D. Ferry, "Viscoelastic Properties of Polymers", 2nd ed., Wiley, New York, N.Y., 1970, Chapter 17, p 99.
 28. J. D. Ferry, *ibid.*, 1970, p 524.
 29. R. Chasset and P. Thirion, personal communication.
 30. P. J. Flory, *J. Amer. Chem. Soc.*, **58**, 5222 (1956).