Mechanical Properties of Substances of High Molecular Weight. II. Rigidities of the System Polystyrene–Xylene and their Dependence upon Temperature and Frequency

BY JOHN D. FERRY

Systems containing materials of high molecular weight frequently have peculiar mechanical properties, which are of interest not only in characterizing the macromolecular components, but also in evaluating their structure and molecular behavior. For example, the viscosities of long chain polymers have been studied extensively, both in solution[1] and in the absence of solvents.[2] The elastic properties of such systems, however, have received little attention.

When the molecular weight of a polymer is sufficiently high, its solutions (in a solvent with which it is miscible in all proportions) grade uniformly from viscous solutions through gelatinous or rubberlike consistencies to plastic solids. The mechanical properties depend markedly upon the concentration and the molecular weight, and also upon the nature of the intermolecular forces between polymer and solvent.

The modulus of elasticity and modulus of rigidity of such a system can be measured only if the mechanical relaxation times are long compared with the time required to complete an experiment. Otherwise the applied stresses are relieved by internal readjustment, i. e., flow, before elastic deformation can be measured. In certain solutions of high polymers, the relaxation times range from the order of a second to very much less. From a static standpoint, when subjected to slow deformation, they behave as liquids of moderately high viscosity. But from the standpoint of rapidly oscillating deformations they behave as rigid solids.

By studying the propagation of transverse vibrations through such solutions, the modulus of rigidity can be determined as a function of frequency, in the transition range between viscous behavior and elastic behavior. The damping also can be observed.

In the present paper, data are given for the propagation of transverse vibrations through solutions of polystyrene in xylene, in which the

concentration of polymer ranges from 15.3 to 52.3%. Xylene was selected as a solvent because of its resemblance to the monomeric unit; toluene would have been more closely similar, but less convenient because of its greater volatility. The rigidities are calculated from the velocities of wave propagation. The dispersion and damping are described and interpreted in terms of stress relaxation. In the following paper,[3] viscosity measurements on the same solutions are reported, and a general description of the mechanical properties is evaluated in terms of molecular behavior.

Theory

A solid body possesses rigidity, i. e., supports a shearing stress, and consequently transmits transverse vibrations, which cannot be propagated in fluids. The modulus of rigidity, G, is defined as

$$G = \mathfrak{T}/\gamma \qquad (1)$$

where $\mathfrak{T}$ is the shearing stress producing an angular deformation (or strain) γ. The velocity of propagation, V, of transverse vibrations in a solid is related[4] to G, as follows

$$G = V^2\rho \qquad (2)$$

where ρ is the density of the solid.

When a solid is maintained at constant strain for a duration comparable with the mechanical relaxation times characteristic of the material, the stress which is required to maintain the strain diminishes. To describe this behavior, Maxwell[5] proposed the function

$$\mathfrak{T} = \mathfrak{T}_0 e^{-t/\tau} \qquad (3)$$

where $\mathfrak{T}_0$ is the initial shearing stress and $\mathfrak{T}$ that at time t. Here the relaxation of stress is characterized by a single time constant, τ. For numerous systems hitherto studied,[6] such as metallic lead, gelatin gels, and dilute solutions of benzopurpurin, it has been impossible to represent the decrease in stress by a single exponential term as

(1) Staudinger, "Die hochmolekularen organischen Verbindungen," Julius Springer. Berlin, 1932; Baker, Fuller and Heiss, THIS JOURNAL, **63**, 3316 (1941).

(2) Flory, THIS JOURNAL, **62**, 1057 (1940); Kauzmann and Eyring, ibid., **62**, 3113 (1940); Ferry and Parks, Physics, **6**, 356 (1935).

(3) Ferry, THIS JOURNAL, **64**, 1330 (1942).

(4) Timoshenko, "Theory of Elasticity," McGraw-Hill Book Co., New York, N. Y., 1934; Coker and Filon, "Photoelasticity," Cambridge Univ. Press, 1931.

(5) Maxwell, Phil. Trans. Roy. Soc., **157**, 52 (1867); Phil. Mag. [4] **35**, 133 (1868).

(6) Michelson, J. Geol., **25**, 405 (1917); Hatschek, "The Viscosity of Liquids," G. Bell and Sons, London, 1928, pp. 224–227.

in (3). In our polystyrene solutions, the Maxwell function has been found adequate to represent within experimental error the dispersion of rigidity, although the measurements are not accurate enough to make a critical test. The function (3) will be employed as the simplest one from which to develop the theory of propagation of transverse vibrations.

The relation between the stress relaxation function and the dispersion of transverse vibrations is somewhat analogous to that between transient currents and the dispersion of impedance in alternating current circuits.[7] The effect of stress relaxation is introduced into the differential equation for a plane wave propagated in the x-direction by setting[8]

$$\rho \frac{\partial^2 \gamma}{\partial t^2} = G^0 \left(1 - \frac{1}{\tau} \int_0^\infty e^{-i\omega u} - u/\tau \, du \right) \frac{\partial^2 \gamma}{\partial x^2} \quad (4)$$

where $\omega = 2\pi\nu$, ν being the frequency of a sinusoidal periodic stress, and G^0 is the "true" rigidity at high frequencies.

The solution for a progressive wave is assumed to have the form

$$\gamma = \gamma_0 e^{i(\omega t - 2\pi x/\lambda) - x/x_0} \quad (5)$$

where λ is the wave length, and x_0 a critical damping distance. We then obtain for the dispersion of velocity, and hence of rigidity

$$\frac{V^2(\omega)}{(V^0)^2} = \frac{G(\omega)}{G^0} = \frac{2\omega^2\tau^2}{\omega^2\tau^2 + \omega\tau\sqrt{1 + \omega^2\tau^2}} \quad (6)$$

The critical damping distance, x_0, is given by

$$x_0 = (\lambda/2\pi)(\omega\tau + \sqrt{1 + \omega^2\tau^2}) \quad (7)$$

It follows that, with decreasing frequency, when $G(\omega)$ has fallen to $G^0/2$, $\omega\tau = 0.36$, and $x_0 = 0.23 \lambda$. The amplitude accordingly falls off in a distance of one wave length by a factor of $e^{-1/0.23}$. This would be below the limit of detection in our apparatus, where strain can be observed with an accuracy of about 5%.

We have not, in fact, been able to make any measurements at frequencies lower than those corresponding to $G/G^0 = 1/2$. Damping has been studied only at the higher frequencies, where the amplitude falls off slowly enough to allow observation over several wave lengths. Unfortunately the limits of the apparatus have not permitted measurements of dispersion and damping on the same solutions.

At the critical frequency, where $\omega\tau = 1$, the

value of G/G^0 is 0.83, and the critical damping distance according to Eq. 7 would be 0.39 λ. Measurements of rigidity would then be possible down to frequencies somewhat lower than the critical frequencies. In our apparatus, for which the one-dimensional Eq. 5 may be considered qualitatively applicable, this has been the case.

Materials

The polystyrene employed was supplied through the kindness of the Dow Chemical Company. It was characterized as Styron A-200, and its molecular weight was given as 75,000–140,000, with an average of 120,000. No attempt at fractionation was made, since some properties of high polymers are independent of the degree of polydispersion,[9] and a preliminary examination of the dependence of rigidity upon concentration, temperature, and frequency was considered to be of interest even with unfractionated material.

J. T. Baker C. P. xylene was used without further purification.

Solutions were prepared by mixing the approximate weights of polymer and solvent and allowing them to stand for several days. The most concentrated solution (52.3% polymer) required several weeks for the formation of a homogeneous mixture; stirring was impossible, and diffusion of the solvent was the only mixing mechanism. Homogeneity was assured by the absence of irregularity in the wave-fronts in the vibration apparatus. Analysis was made by evaporating weighed portions at 105°, after measurements of rigidity. Concentrations are expressed as weight per cent.

Densities of Solutions.—For the calculation of the modulus of rigidity, the density of the system is required. Coefficients of volume expansion for two concentrated solutions of the polymer (31.8 and 52.3%) were measured by observing the increase in height of liquid in a rectangular glass cell of known dimensions, using the optical system of the rigidity apparatus. The values were within a few per cent. of the coefficient of expansion of pure m-xylene,[10] i. e., 1.00×10^{-3} deg.$^{-1}$ at 25°. By contrast, the volume expansion coefficient of the pure polymer[11] is 0.22×10^{-3}.

The densities could not be measured with sufficient accuracy by this means, so it was assumed that the densities of solutions at 25° varied linearly with the weight fraction from 0.86 for xylene[10] to 1.05 for polystyrene.[11] Negative deviations from linearity may be expected,[12] but this procedure is probably sufficiently accurate for calculations of rigidity. Temperature corrections were then made with the above figure for the expansion coefficient of the solvent.

Method and Procedure

The apparatus for propagation of transverse vibrations was the same as that previously described,[13] with the loud-

(7) Debye, "Polar Molecules," Chemical Catalog Co., New York, N. Y., 1929; Yager, *Physics*, **7**, 434 (1936).

(8) *Cf.* Derjaguine, *Beitr. angew. Geophysik*, **4**, 452 (1934), where the case for spherical waves is treated.

(9) Fuoss, THIS JOURNAL, **63**, 2401 (1941).

(10) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1926.

(11) Personal communication from the manufacturer.

(12) Mark, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, New York, N. Y., 1940.

(13) Ferry, *Rev. Sci. Instruments*, **12**, 79 (1941).

speaker and cell assembly enclosed in an air thermostat. A refrigerating unit, heating coils, a Quickset bimetallic thermoregulator,[14] and a powerful fan for air circulation made it possible to maintain within 0.1° any temperature between −5 and 40°.

The glass cell containing the polymer solution was covered with cellophane, provided with a slit for the vibrator plate; the opening was sealed with a very soft cement made by heating agar-agar with glycerol. The vibrations were produced by a thin glass plate moving in its own plane, driven by a loudspeaker.

The strain double refraction was examined strobo-scopically, employing a Babinet compensator to obtain patterns representing the variation of double refraction (Δ) with distance from the vibrator plate (x). Horizontal and vertical coördinates of maxima and minima were measured. The vertical displacements of the line of zero retardation were reckoned from the base-line for the solution at rest. The double refraction observed in the Babinet (Δ) was corrected to give the double refraction in the strained gel (δ) by the equation[13]

$$-\tan \delta = \tan \Delta \sin 2\alpha \qquad (8)$$

where α is the angle between the axis of the Babinet and the axis of the polarizing Polaroid plate (which is parallel to the plane of motion of the vibrator plate). The angle α was usually about 4°.

The excursion of the vibrator plate, A, was too small to be observed, less than 0.01 mm. The maximum strains, Γ, ($\tan \Gamma = A\pi/\lambda$) were less than 5°. The maximum value of double refraction, δ_0, varied from 10 to 20°. The amplitude was arbitrarily adjusted to give the clearest pattern. No attempt has been made to calculate the strain-optical coefficients.

When the vibration was stopped, the strains disappeared immediately, showing that the relaxation times involved were much less than a second in magnitude.

Each solution was studied between − 5 and 40° at frequencies spaced about equally on a logarithmic scale, ten to a decade. The frequency range for each solution was twofold to eightfold; the entire range covered was from 200 to 4000 cycles.

Results

Form of Vibration Pattern.—At high concentrations and low frequencies, the stroboscopically viewed wave of strain included two to three wave lengths on each side of the vibrator plate. As the frequency was increased, the vibrations were more strongly damped until only one wave length was visible. At lower concentrations (below 25%), scarcely more than one wave length was visible over the whole frequency range.

The wave length was taken as the distance between maxima or between minima on each side of the plate. These values, which agreed to about 5%, and were independent of distance from the source of vibration, were averaged and multiplied by the frequency, ν, to give the velocity of propa-

(14) American Instrument Co., Silver Spring, Md.

gation, V. The modulus of rigidity was calculated by Eq. 2.

For the four solutions of highest concentration, when the number of maxima and minima on each side was four or more, their amplitudes were measured and the corresponding values of δ plotted against x. The curves thus obtained were exponential within experimental error, though the test was not very critical (Fig. 1).
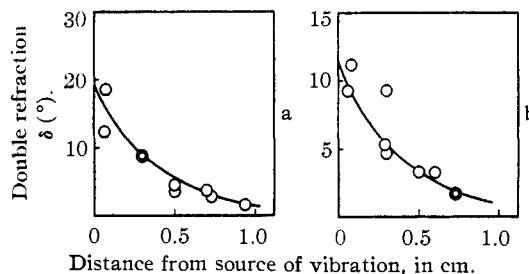

Fig. 1.—Damping of transverse vibrations in polystyrene in xylene: double refraction plotted against distance from source of vibration, at 1000 cycles: (a) 42.2%, 9.7°, in cell (a), $\delta = 19.0 \ e^{-x/0.40}$ (b) 42.5%, 8.5°, in cell (b), $\delta = 11.5 \ e^{-x/0.40}$.

The constancy of λ and the exponential damping of δ support Eq. 5, if δ is proportional to γ (which is a reasonable assumption[15]) and if the system can be considered one-dimensional. The latter consideration involves neglecting the effects of the walls of the cell. To ascertain their influence, the measurements on the 42.2 and 42.5% solutions were made in cells of different cross section (Fig. 2, (a) and (b), respectively). The double refraction observed is, of course, the integral over the thickness of the cell, in the line of sight; and the drag of the walls should cause it to damp more markedly in cell (a) than in cell (b),
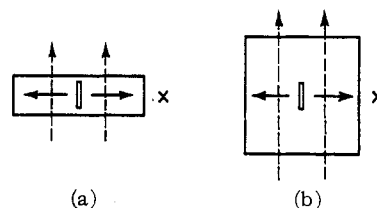

Fig. 2.—Cross sections of cells employed for propagation of transverse vibrations. The solid arrows give the direction of propagation; the dotted arrows the direction of observation (line of sight); the motion of the vibrator plate is perpendicular to the plane of the paper.

(15) This involves the assumption that the double refraction and the strain undergo the same relaxation. Coker and Filon[4] and Farwell [J. Appl. Physics, 11, 274 (1940)] show that in plastic solids this is not the case; but in our solutions, where the relaxation times are very short, it seems plausible. Studies of double refraction of flow may give some information on this point.

wave propagation being in the x-direction. Yet the critical damping distances observed were closely the same (cf. Table II). It is on this basis that the results are interpreted in terms of Eq. 5. All other solutions were studied in cells of the type (a).

Dispersion.—At a concentration of 25.7% at the highest temperature (40.6°), and at lower concentrations at all temperatures studied, the velocity of propagation clearly varied with the frequency, showing dispersion of the rigidity. The results can be fitted to Eq. 6, but are not very conclusive (Fig. 3). The values of G^0 were estimated by plotting G against G/ν^2, which should give a straight line at high frequencies, and extrapolating to $G/\nu^2 \rightarrow 0$. The ratios G/G^0, plotted logarithmically against frequency, were then superposed on a standard plot of Eq. 6, to find the frequency at which $\omega\tau = 1$, in order to estimate the relaxation time. Composite graphs of G/G^0 against $\omega\tau$ are given in Fig. 3 for the 15.3% and the 20.6% and 21.3% solutions.
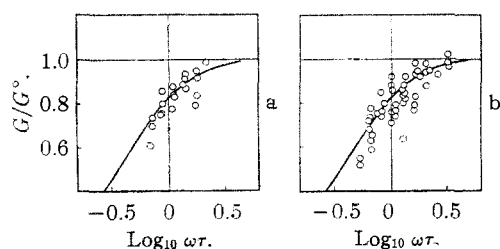

Fig. 3.—Dispersion of rigidity for transverse vibrations: points, experimental values of G/G°; curves, equation (6); (a) 15.3%; (b) 20.6 and 21.3%.

The values of τ thus estimated are given in Table I. They are all of the order of 4×10^{-4} second, and exhibit surprisingly little variation with temperature or composition.

TABLE I

RELAXATION TIMES ESTIMATED FROM DISPERSION ON THE BASIS OF EQUATION (6)

Concn. polystyrene, %	Temp., °C.	$\tau \times 10^4$, sec.	Concn. polystyrene, %	Temp., °C.	$\tau \times 10^4$, sec.
15.3	−4.7	3.5	20.6	10.8	4.1
	8.6	3.5		17.2	4.1
	14.0	3.5		22.7	4.2
	25.4	3.5		39.8	3.2
	28.3	3.5	21.3	31.2	3.5
			25.7	40.6	5.1

Damping.—The critical damping distances observed in the three solutions of highest concentration were all of the order of one wave length.

From the critical damping distance, according to Eq. 7, the relaxation time is calculated as

$$\tau = \pi x_0/\omega\lambda - \lambda/4\pi\omega x_0 \qquad (9)$$

and it follows that at the frequencies employed $\omega\tau \simeq 3$. It is important to check the constancy of τ as given by (9) over a wide range of frequencies, to test the applicability of the theory. Thus far, however, the number of observable maxima and minima has been limited by the width of the cell at low frequencies and by the increased damping at high frequencies; so that it has not been possible to measure x_0 over a frequency range of more than twofold, which is inadequate. Hence, although there was in some cases a diminution of τ with increasing frequency, this was ignored and the values were averaged for the purposes of calculation, pending a more extensive study.

The results are given in Table II. These relaxation times calculated from the damping, for concentrated solutions, are also of the order of 4×10^{-4} second, and show little if any trend with temperature. There is some decrease with increasing concentration, but compared with the concentration dependence of the rigidity itself, and of the viscosity,[3] the variation is small.

TABLE II

RELAXATION TIMES ESTIMATED FROM DAMPING ON THE BASIS OF EQUATION (7)

Concn. polystyrene, %	Temp., °C.	$\tau \times 10^4$, sec.	Concn. polystyrene, %	Temp., °C.	$\tau \times 10^4$, sec.
31.8[a]	8.3	8.1	42.5[b]	−5.0	4.2
	20.1	7.7		8.5	5.1
	24.7	6.5		26.1	4.5
	29.2	6.7			
			52.3[a]	2.6	2.5
42.2[a]	−0.7	4.8		8.0	2.6
	4.5	4.5		16.5	3.0
	9.7	4.0		22.9	4.2
	21.6	3.8		31.1	3.8
	25.3	4.6			

[a] Cell (a).   [b] Cell (b).

Modulus of Rigidity.—Where dispersion occurred, the modulus of rigidity was taken as G^0, determined as described above. For all other solutions, the velocity of propagation, which was sensibly independent of the frequency, was averaged at each temperature over the frequency range covered. The agreement was within about 5%, except for a few cases at low temperatures where a rise of up to 10% occurred in the high frequency range; these high values were discarded.

The velocities of propagation and the loga-

rithms of modulus of rigidity are given in Table III, and the latter are plotted in Fig. 4 against

TABLE III
VELOCITY OF TRANSVERSE VIBRATIONS AND MODULUS OF RIGIDITY FOR SOLUTIONS OF POLYSTYRENE IN XYLENE

Concn. polystyrene, %	Temp., °C.	V^0, cm./sec.	$\mathrm{Log_{10}}\ G^0$ (dyne cm.$^{-2}$)
15.3	– 4.7	109	4.04[a]
	– 2.2	110	4.04[a]
	8.6	98	3.94[a]
	14.0	106	4.00[a]
	25.4	93	3.88[a]
	28.3	97	3.91[a]
20.6	10.8	153	4.33[a]
	17.2	146	4.28[a]
	22.7	149	4.30[a]
	39.8	148	4.29[a]
21.3	31.2	152	4.32[a]
25.7	– 6.0	205	4.60
	– 3.0	200	4.57
	5.4	195	4.55
	10.0	193	4.54
	16.1	193	4.53
	20.2	184	4.49
	25.0	185	4.49
	31.5	173	4.43
	40.6	175	4.43[a]
31.8	– 2.1	293	4.91
	8.3	277	4.86
	12.5	260	4.80
	16.7	271	4.83
	20.1	260	4.79
	24.7	252	4.77
	29.2	252	4.76
36.0	1.4	355	5.08
	10.4	334	5.02
	18.8	324	4.99
	29.1	326	4.99
	36.5	308	4.94
	43.0	299	4.91
42.2	– 5.7	491	5.37
	– 5.5	494	5.37
	– 0.7	452	5.30
	4.5	450	5.29
	9.7	437	5.26
	14.2	424	5.23
	20.6	419	5.22
	21.6	416	5.21
	25.3	414	5.21
	30.2	416	5.21
42.5	– 5.0	438	5.27
	0.3	437	5.27
	5.2	409	5.21
	8.5	420	5.23
	14.8	406	5.20
	18.0	404	5.19
	21.7	408	5.20
	26.1	402	5.18
52.3	– 2.0	918	5.92
	2.6	784	5.78
	8.0	736	5.72
	16.5	685	5.65
	22.9	646	5.60
	31.1	624	5.57

[a] Extrapolated to high frequency.

the reciprocal of the absolute temperature. They cover the wide range of 10^4 to 10^6 dyne cm.$^{-2}$. Except for the three solutions of highest concentration, the curves are linear and of nearly constant slope. Thus the temperature variation of the rigidity follows the formula $G = A_G e^{-Q_G/RT}$. The heat Q_G is about 1.5 kilocalories, independent of concentration up to 40%.
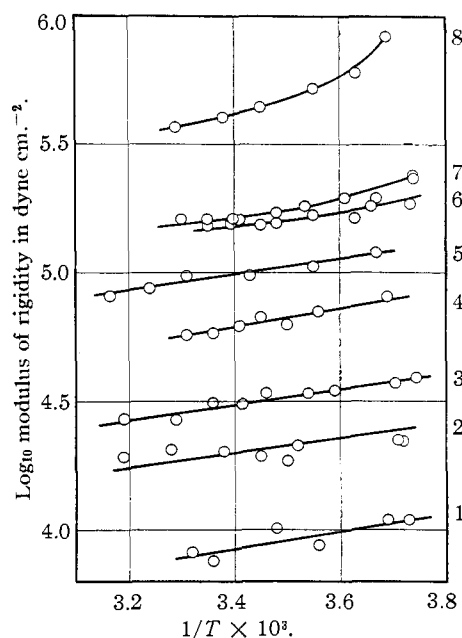

Fig. 4.—Logarithm of the modulus of rigidity plotted against $1/T$: 1, 15.3%; 2, 20.6 and 21.3%; 3, 25.7%; 4, 31.8%; 5, 36.0%; 6, 42.5% (cell b); 7, 42.2%; 8, 52.3%.

The sharper rise of rigidity at low temperatures in the 52.3% solution may be the beginning of the "brittle point." This transition occurs in unplasticized polystyrene[11] at about 80°. In the case of polyvinyl chloride,[16] the addition of 20% plasticizer (diphenyl) lowers the brittle point from 70 to 30°. In our polystyrene solution, the presence of 50% plasticizer (xylene) may depress the brittle point to about –10°, so that our lowest temperature employed is just at the top of the transition. This is further suggested by the value of G here—10^6 dyne cm.$^{-2}$, or 15 lb. per sq.

(16) Fuoss, THIS JOURNAL, **63**, 378 (1941); Fig. 13.

in.—which is near where the brittle point begins in a polyvinyl chloride plastic of comparable composition.[16]

Modulus of Elasticity.—The modulus of elasticity, E, is given[4] by

$$E = 2G(1 + \mu) \qquad (10)$$

where μ is Poisson's ratio. The latter is always close to $1/2$ when the product of the elasticity or the rigidity and the compressibility, κ, is much less than unity, as is shown by the relation[4] $1 - 2\mu = \kappa E/3$. The compressibility of the polystyrene solutions is undoubtedly no higher than that of the solvent, 10^{-8} dyne^{-1} cm.$^{-2}$, and μ is therefore very nearly $1/2$. The elastic modulus is accordingly equal to $3G$.
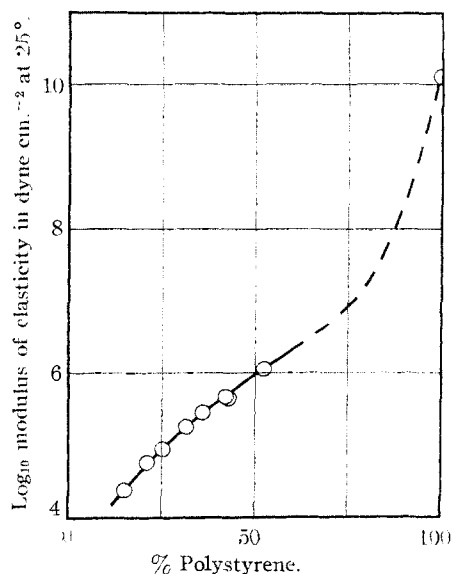

Fig. 5.—Logarithm of the modulus of elasticity at $25°$ plotted against composition.

Values of the modulus of elasticity at $25°$ are given in Table IV and plotted against the composition in Fig. 5. Here the value for pure polystyrene[11] is also included. It will be of interest to

TABLE IV

MODULUS OF ELASTICITY OF THE SYSTEM POLYSTYRENE-XYLENE AT $25°$

Concn. polystyrene, %	$\mathrm{Log_{10}} E$ (dyne cm.$^{-2}$)
15.3	4.39
21.0	4.78
25.7	4.95
31.8	5.25
36.0	5.46
42.2	5.69
42.5	5.66
52.3	6.06
100	10.11

study the remainder of the concentration range, through which the dotted curve is extended. An inflection may be expected if a room temperature brittle point occurs in this region.

Discussion

It is striking that rigidities of considerable magnitude can be demonstrated by oscillating deformation in systems which give no hint of solidity in visual examination. The 15% polystyrene solution, which appears to be a moderately viscous liquid ($\eta = 15$ poises), has the rigidity of a fairly stiff gelatin gel. The 50% solution, which shows some elastic retraction but flows with no yield point, has about the rigidity of raw rubber. The small relaxation times prevent these rigidities from being perceived in static deformation.

It is of interest to compare our results with the observations of Kendall,[17] who studied the transient resilience of dilute solutions of various polymers, subjected to a shearing impulse of very short duration (10^{-5} to 3.5×10^{-4} sec.). In a solution of polybutene of molecular weight 80,000 and viscosity 16 poises (the concentration is not given, but the viscosity is comparable with that of 15.3% polystyrene), the modulus of rigidity was estimated from the elastic recoil as about 10^4 dyne cm.$^{-2}$—in agreement with that of 15.3% polystyrene. The recoil time increased with increasing amplitude of shear, and was of the order of 10^{-2} to 10^{-3} sec. The elastic recoil persisted at greater dilutions, but disappeared below concentrations corresponding to viscosities of 0.25 to 0.15 poise. With this type of method, it should be possible to study mechanical characteristics of polymer solutions associated with possible relaxation times intermediate between those described in the present paper (4×10^{-4} sec.) and those derived from the viscosity measurements of the following paper (10^{-2} to 10^2 sec.)

The fact that the rigidity of our polystyrene solutions decreases with increasing temperature shows that it must be due primarily to intermolecular forces rather than to the entropy of strain orientation. The latter effect, associated with the uncurling of chain molecules from their most probable configurations, should produce a rigidity which increases with temperature and is in fact proportional to the absolute temperature.[18,19]

(17) Kendall, *Rheology Bulletin*, **12**, 26 (1941).

(18) Guth and Mark. *Monatsh.*, **65**, 93 (1934); Mark, *J. App. Phys.*, **12**, 41 (1941).

(19) Kuhn. (a) *Kolloid Z.*, **76**, 258 (1936); (b) **87**, 3 (1939).

It is possible, however, that a part of the rigidity may be due to the strain orientation effect, and the remainder can be attributed to a transfer of stress by intermolecular forces. By postulating two mechanisms in this way, the magnitude of the temperature dependence can be explained qualitatively. If any quantity proportional to T (like the strain orientation rigidity) is plotted logarithmically against $1/T$ in a small temperature range, a fictitious heat effect of $-RT$ can be deduced. In our temperature range, this amounts to about -0.6 kcal. The heat effect which is associated with van der Waals forces, and determines the temperature dependence of the viscosity of non-polar liquids, for example, is about 2 kcal. The presence of both mechanisms may account for the observed Q_G of 1.5 kcal.

Relaxation Times.—It is surprising that the dispersion of rigidity appears sufficiently sharp to be represented in terms of a single relaxation time, in view of the very broad dispersions found by Fuoss for the electrical properties of high polymer solutions. His solutions of polyvinyl chloride and polychlorostyrene were in a more concentrated range, it is true (40–100% polymer), and their dielectric dispersion became sharper with decreasing concentration; but it does not appear that a Debye function would be attained even at infinite dilution. The theory of Kirkwood and Fuoss[20] predicts a rather broad dispersion at infinite dilution, on the basis of relaxation through internal rotatory Brownian motion. However, the molecular motions involved in the electrical relaxations consist of the orientation of dipoles attached to the polymer chains. The motions involved in the relaxation of the two rigidity mechanisms we postulate—strain orientation and the support of stress by intermolecular forces—are probably quite different.

It is also surprising that the relaxation times calculated from dispersion and damping are nearly independent of temperature and composition. Here, again, the behavior deviates from that of the electrical properties of polyvinyl chloride. In the measurements of Fuoss upon solutions of that polymer,[16,21] the reciprocal of the frequency of maximum dielectric loss (representing a mean relaxation time) undergoes a very marked variation with temperature (associated with a heat of about 40 kcal.) and with composition. It is not possible to make corresponding electrical measurements upon our polystyrene solutions, which contain no polar groups.

The small magnitude of τ — 4×10^{-4} sec.— and its independence of concentration suggest that it cannot be associated with strain orientation, at least if the latter involves orientation or uncurling of long segments of molecules, and is most probably connected with the transfer of stress by intermolecular forces. This interpretation is more fully discussed in the following paper, in which viscosity measurements are reported.

Summary

1. Solutions of polystyrene in xylene, which in static deformation appear to be viscous liquids with no yield value, support transverse vibrations and therefore possess rigidity.

2. The propagation of transverse vibrations in such solutions has been studied over a concentration range of 15.7 to 52.3% polymer and a temperature range of -5 to $40°$, between frequencies of 200 and 4000 cycles.

3. The dispersion of velocity at low concentrations and the damping at high concentrations are described. Both phenomena are analyzed in terms of a single relaxation time of about 4×10^{-4} sec., which is independent, to a first approximation, of temperature and composition.

4. The modulus of rigidity varies from 10^4 to 10^6 dyne cm.$^{-2}$ in the range studied. Its decrease with increasing temperature is characterized by a heat effect of 1.5 kcal.

5. The results are discussed in terms of the molecular behavior of long chain polymers.

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(20) Kirkwood and Fuoss, *J. Chem. Phys.*, **9**, 329 (1941).

(21) Fuoss, THIS JOURNAL, **63**, 2410 (1941).