Mechanical Properties of Substances of High Molecular Weight. III. Viscosities of the System Polystyrene–Xylene

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In the preceding paper,[1] the propagation of transverse vibrations through solutions of polystyrene in xylene was described, and the modulus of rigidity calculated as a function of concentration and temperature. At the lower concentrations, the dispersion of the rigidity was measured, and, at higher concentrations, the damping was observed. Both these phenomena were interpreted in terms of a single relaxation time.

In order to make a more complete description of the mechanical properties of this system, and to attempt to relate them to molecular mechanisms, viscosity measurements have been made on the same solutions.

The viscosity is in every case dependent on the rate of shear. At the higher concentrations, the solutions exhibit elastic recoil. These phenomena have been studied. Values for the viscosity (extrapolated to zero shear), and its temperature coefficient, are given for concentrations up to 52.3% polymer.

Materials

The sources of materials, and methods of preparation and analysis of solutions, were the same as in the previous paper. The molecular weight of the polystyrene was given by the manufacturer[2] as 75,000–140,000, with an average of 120,000. Concentrations are expressed as weight per cent.

Method

A Stormer viscosimeter[3] was employed, with specially constructed cylinders. The outer, of chromium-plated brass, had a diameter of 3.5 cm. and a depth of 6.9 cm. The inner (rotor) was a glass cylinder 1.6 cm. in diameter and 2.6 cm. high, suspended on a glass rod 0.4 cm. in diameter. The low heat conduction of the latter permitted temperature control between 1° and 30° by circulation of water around the outer cylinder. At the lower viscosities, revolutions were counted; at the highest viscosities, rotation was followed by a mirror attached to the rotor and a scale and telescope. The elastic recoil was also measured by this device. Ample time was allowed for the rate of rotation to attain a constant value before measurements were begun.

The apparatus was calibrated by samples of standardized castor oil and of lubricating oil, each at two different tem-

peratures.[4] The volume of liquid was 40 cc. These materials showed Newtonian behavior; the curves of revolutions per second (n/t) against load (w) were straight lines passing through the origin. When the reciprocal slopes of these lines, $w/(n/t)$, were plotted against the respective viscosities (which ranged from 7.2 to 440 poises) a straight line was obtained which passed through the origin. From the constant ratio of viscosity to $w/(n/t)$ thus obtained, the apparatus constant was evaluated as 0.684 poise rev. sec.$^{-1}$ g.$^{-1}$, which was used in all subsequent determinations. As a confirmation in order of magnitude, the value calculated from the dimensions of the cylinders,[5] neglecting end-effects and frictional corrections, was 0.77.

The rate of shear varied in this apparatus from 16.0 (n/t) at the inner cylinder to 3.4 (n/t) at the outer cylinder. As a rough measure, the average rate of shear can be taken as the geometric mean, 7.3 (n/t) sec.$^{-1}$.

Measurements were made on five polystyrene solutions, each at four or five different temperatures, and, at each temperature, at three or more different rates of shear.

Results

Dependence of Apparent Viscosity upon Load. The rate of rotation per unit load, $(n/t)/w$, increased linearly with the load in all cases, so that the consistency curves $(n/t$ against $w)$ were parabolas; the apparent viscosity could be expressed by the equation

$$1/\eta' = (1/\eta)(1 + bw) \qquad (1)$$

where η' is the apparent viscosity for a load w, and η the extrapolated viscosity at zero load.[6] This is illustrated by Fig. 1, where the reciprocals of apparent viscosities of a 25.7% solution are plotted against the load. Although anomalous viscosity is commonly considered a function of the rate of shear, rather than of the shearing stress, we have employed Eq. 1 as the most convenient extrapolation function, since neither the apparent viscosity nor its reciprocal was found to be a linear function of the average rate of shear.

The constant b showed no trend with temperature (except for a slight increase with decreasing temperature at the lowest concentration studied).

(1) Ferry, THIS JOURNAL, **64**, 1323 (1942).

(2) The Dow Chemical Company, Midland, Michigan, to whom we are much indebted for supplying this material.

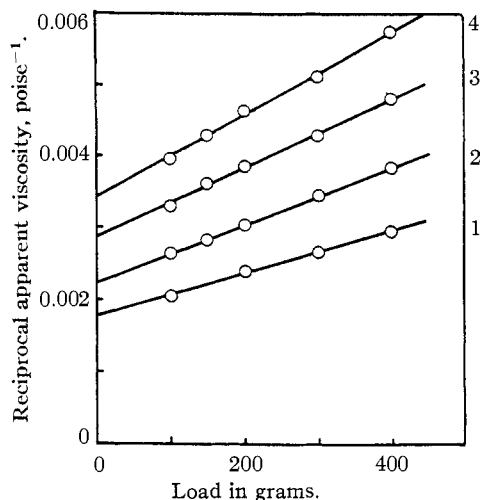(3) Sold by the Central Scientific Company.

(4) We are much indebted to Prof. E. A. Hauser of the Massachusetts Institute of Technology for the standardized castor oil, and to Prof. J. C. Balsbaugh for the standardized lubricating oil. Also we wish to thank Dr. Charles R. Harmison, who carried out the calibration measurements, in connection with studies of the viscosity of concentrated casein solutions, to be reported subsequently.

(5) Hatschek, "The Viscosity of Liquids," G. Bell and Sons, London, 1928, p. 54.

(6) Ferry and Parks, Physics, **6**, 356 (1935).

Fig. 1.—Dependence upon load of the apparent viscosity of polystyrene–xylene solutions: $1/\eta'$ plotted against the load in grams, at a concentration of 25.7%: 1, 1.5°; 2, 9.8°; 3, 17.6°; 4, 24.0°.

The average values at five different concentrations are given in Table I.

Although the shearing stress in the apparatus varies with radial distance, a measure of the average stress can be obtained by multiplying the average rate of shear, estimated above, into the apparatus constant. This gives for stress (in dyne cm.$^{-2}$) $\mathfrak{C} = 5.0w$, where w is in grams. On this basis, we rewrite (1) as

$$\eta' = \eta/(1 + b'\mathfrak{C}) \qquad (2)$$

Values of b' are also given in Table I. It is interesting that these parameters are inversely proportional to the concentration, up to over 30%, as shown in Fig. 2.

TABLE I

CONSTANTS CHARACTERIZING DEPENDENCE OF APPARENT
VISCOSITY UPON LOAD

Concn. polystyrene. %	$b \times 10^3$ g.$^{-1}$	$b' \times 10^4$. dyne^{-1} cm.^{2}
15.4	3.0	6.0
21.0	2.4	4.8
25.7	1.7	3.4
31.8	1.4	2.8
52.3	0.4	0.8

Viscosities Extrapolated to Zero Load.—The values for the viscosity extrapolated to zero load are given in Table II. The logarithms of viscosities are plotted against the reciprocal of the absolute temperature in Fig. 3, showing a linear relation in each case. The interpolated viscosities at 25°, as well as the values of the heat of activation for viscous flow, $Q_\eta (= R \, d \ln \eta / d(1/T))$, are given in Table III and plotted in Figs. 4 and
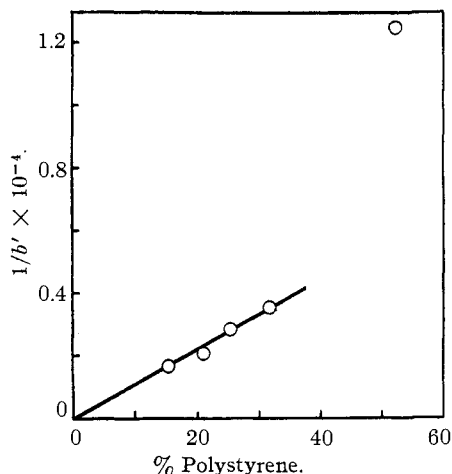

Fig. 2.—Parameter $1/b'$, characterizing dependence of viscosity upon shearing stress, plotted against the concentration.

5. Here the figures for pure m-xylene[7] are also included. The viscosity covers the enormous range of 10^{-2} to 10^5 poises in the concentration range studied. Its logarithm shows marked positive deviations from a linear variation with con-

TABLE II

VISCOSITIES OF SOLUTIONS OF POLYSTYRENE IN XYLENE
EXTRAPOLATED TO ZERO LOAD

Concn. polystyrene, %	Temp., °C.	η poises	Concn. polystyrene, %	Temp., °C.	η poises
15.4	1.0	27.9	31.8	1.1	2,270
	9.7	22.6		7.8	1,790
	15.4	19.5		11.7	1,450
	21.7	16.6		18.6	1,170
	24.8	16.2		25.1	1,000
21.0	1.6	145.8	52.3	2.7	506,000
	11.6	109.0		9.9	285,000
	14.8	97.5		16.7	180,000
	20.4	82.6		25.0	116,000
	24.9	78.7		30.5	94,000
25.7	1.5	565			
	9.8	450			
	17.6	348			
	24.0	291			

TABLE III

VISCOSITIES AND HEATS OF ACTIVATION OF SOLUTIONS OF
POLYSTYRENE IN XYLENE AT 25°

Concn. polystyrene, %	η poises	Q_η, cal.
0	0.0059	2,100
15.4	15.5	3,800
21.0	74.0	4,600
25.7	282	4,600
31.8	995	5,300
52.3	116,000	10,700

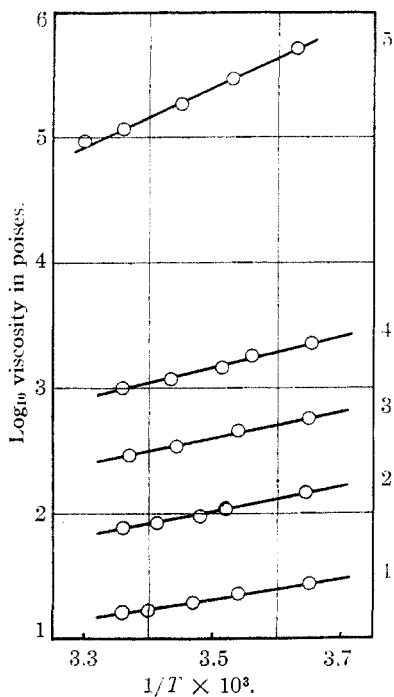(7) Landolt-Börnstein. "Tabellen." 5 Auflage, 1923.

Fig. 3.—Viscosity of polystyrene–xylene solutions, extrapolated to zero load, plotted logarithmically against $1/T$: 1. 15.4%; 2. 21.0%; 3. 25.7%; 4. 31.8%; 5. 52.3%.

centration. The heat of activation apparently increases linearly at first, then more rapidly at very high concentrations.

Measurements of Elastic Return.—The more concentrated solutions exhibited elastic recoil, the viscosimeter rotor reversing its motion when the load was removed. For the 52.3% solution, the recovery was followed with time. Curves of which Fig. 6 is typical were obtained. These provide two types of information: the total recovery, which is related to the elastic properties of the system; and a time function related to a relaxation mechanism of some kind.

The total recovery was approximately proportional to the load. From the ratio of load to this recoverable deformation, using the same apparatus constant as for the viscosity calculation, a modulus of rigidity can be derived. This is not, of course, the true modulus of rigidity, measured at high frequencies, but represents the recoverable deformation under the conditions of steady flow. Values (G') for five temperatures are given

TABLE IV

MODULUS OF RIGIDITY CALCULATED FROM RECOVERABLE DEFORMATION IN STEADY FLOW

(52.3% Polystyrene)

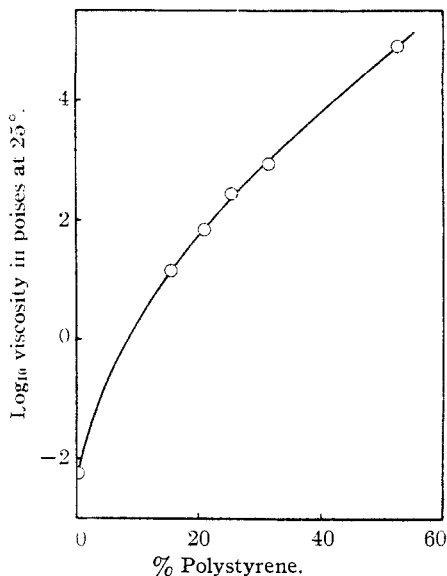| Temp., °C.	2.7	9.9	16.7	25.0	30.5
$G' \times 10^{-4}$	1.4	0.9	0.9	0.9	0.9

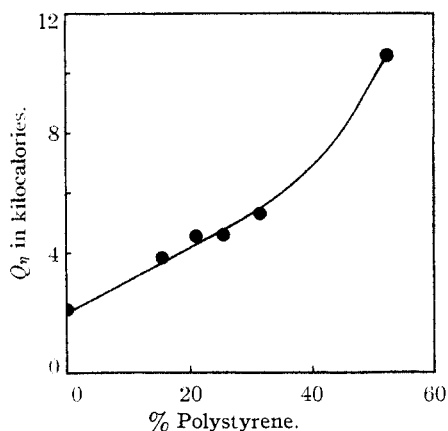Fig. 4.—Logarithm of viscosity at 25° plotted against concentration.

Fig. 5.—Heat of activation, Q_η, plotted against concentration.

(in dyne cm.$^{-2}$) in Table IV. They are very much smaller than the true (high-frequency) rigidity.

The curves of angle of recovery against time resemble similar creep recovery data for a wide variety of systems[8] in that they cannot be fitted by exponential functions. Only sums of several exponential terms could suffice, covering a broad distribution of time constants. Without an attempt to analyze the recoil function, the order of magnitude of the recoil times may be characterized by the time at which $(e - 1)/e$ of the recovery is accomplished, which amounts to fitting an exponential curve to three points (dotted curve in Fig. 6). The values thus obtained (τ_r) decreased

(8) Silk: Weber, Ann. Physik. **34**, 247 (1835); glass: Kohlrausch, ibid., **119**, 337 (1863); steel: Van Orstrand, Bull. Geol. Soc. Am., **34**, 300 (1923); boron trioxide: Griggs, J. Geol., **47**, 225 (1939).
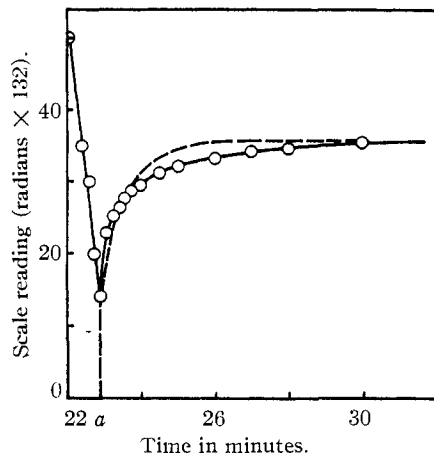
Fig. 6.—Recovery of deformation after steady flow. 52.3% polystyrene at 9.9°; load 400 g. Scale divisions are plotted against time. The load was removed at a.

with increase in the original load, probably because the distribution of time constants was altered. When extrapolated to zero load, the times τ_r ranged from 28 sec. at 30.5° to 98 sec. at 2.7°. These figures are enormously greater than the relaxation times deduced from the dispersion and damping of transverse vibrations, in the preceding paper. They are plotted logarithmically against $1/T$ in Fig. 7, and the slope of the curve represents a heat effect $(Q_{\tau_r} = R \, d \ln \tau_r/d(1/T))$ of 9.3 kcal. This is close to Q_η at the same concentration (10.7 kcal.).

Discussion

A number of remarks can be made on these results before they are combined with the rigidity data of the preceding paper.

Dependence of Viscosity upon Concentration. —The curve of Fig. 4 has roughly the form predicted by Powell, Clark and Eyring,[9] who have proposed the equation for solutions of a linear polymer

$$\log \eta = (1 - \varphi) \log \eta_0 + (1 - \varphi) \log (1 + kz\varphi) + \varphi \log \eta_P \quad (3)$$

Here η, η_0, and η_P are the viscosities of solution, solvent, and pure polymer, respectively, φ is the volume fraction of polymer, z is the chain length, and k is a constant characteristic of a polymer species.

In our case, τ_P is unknown (it would have to be extrapolated from high temperature measurements above the brittle point)[1]; however, the only other unknown is kz, and Fig. 4 can be fitted by

(9) Powell, Clark and Eyring, presented at the New York Academy of Sciences, February, 1941.
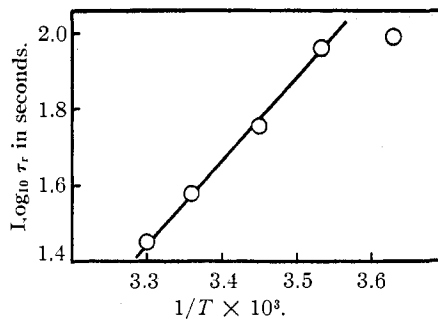

Fig. 7.—Mean recoil time at 52.3% concentration, extrapolated to zero load, plotted logarithmically against $1/T$.

taking $\log \eta_P = 9.57$ and $kz = 1770$, as Table V shows. (The densities have been calculated as described in the previous paper.)

TABLE V

VISCOSITY AT 25° CALCULATED FROM EQUATION (3), WITH $\log \eta_P = 9.57$ AND $kz = 1770$

Volume fraction	Weight fraction	Log η calcd.	Log η obsd.
0.1	0.12	0.99	0.70
.2	.23	2.16	2.15
.3	.34	3.21	3.26
.4	.45	4.20	4.23
.5	.55	5.15	5.12

The value of kz thus deduced from very high concentrations may be compared with that determined in dilute solution. Here[9] $\eta = \eta_0(1 + kz\varphi)$, and by identification with the Staudinger relationship, $\eta = \eta_0(1 + K_m Mc)$, where c is the concentration expressed as moles of monomer per liter and K_m is the Staudinger constant, we have $kz = K_m \rho n \times 1000$, where ρ is the density of polymer and n the degree of polymerization. For our material,[1] $\rho = 1.05$, $n = 1.1 \times 10^3$, and K_m is given[10] as 1.8×10^{-4}. This yields $kz = 220$, which is about one-eighth of the value obtained at high concentrations.

Dependence of Viscosity upon Temperature.— If the linear portion of Fig. 5 is extrapolated to 100% polymer, a value of 12 kcal. is obtained for the heat of activation for viscous flow of the pure polystyrene. This is of the same order as that calculated by Smallwood[11] for rubber (11 kcal.) and by Flory[12] for synthetic polyesters (8 kcal.). Actually, the heat Q_η rises more rapidly at high concentrations, so that the extrapolated value is nearly attained at a concentration of 50%. This rise may be in anticipation of a room tem-

(10) Personal communication from the manufacturer.
(11) Smallwood, J. Appl. Physics, 8, 505 (1937).
(12) Flory, THIS JOURNAL, 62, 1059 (1940).

perature brittle point somewhere above 50% concentration. Such a brittle point is also suggested by the rigidity measurements.[1]

Dependence of Viscosity upon Rate of Shear.— When a polymeric solution undergoes steady flow, there is not only a constant *rate* of strain externally, but the system is in a state of internal strain which does not change with time. Obvious indications of this internal strain are double refraction of flow and the elastic recoil upon removal of load. The potential energy of the strain may in some cases be entirely represented by decrease of entropy through orientation; in other cases it may involve stretched bonds or strained bond angles. The internal strain, γ_a, may be defined formally as

$$\gamma_a = \mathfrak{T}/G_a \qquad (4)$$

where $\mathfrak{T}$ is the shearing stress which is simultaneously producing external flow, and G_a is an internal modulus of rigidity.

In extremely dilute solutions of anisotropic molecules, the dependence of viscosity upon rate of shear is readily attributed to orientation and can be treated by hydrodynamics. For our far more concentrated systems, we shall not attempt a microscopic analysis, but merely assume that the viscosity depends upon the internal strain, so that $\eta' = \eta f(\gamma_a)$. The empirical Eq. (2) suggests that f is of the form[13]

$$\eta' = \eta/(1 + \gamma_a) = \eta/(1 + \mathfrak{T}/G_a) \qquad (5)$$

and identifies the empirical constant b' with $1/G_a$.

Taking the values of b' from Table I, we find, at a concentration of 52.3%, $G_a = 1.2 \times 10^4$ dyne cm.$^{-2}$. This is in very satisfactory agreement with the values of G' (Table IV) calculated from elastic recoil, and identifies the two moduli G_a and G'. A possible connection between the phenomena of anomalous viscosity and elastic recoil is thereby established.

The inverse proportionality of b' with concentration at low concentrations thus means that G_a, or G', is proportional to the concentration

$$G_a = G' = 1.1 \times 10^4 g \qquad (6)$$

where g is the weight fraction.

The theoretical contribution to rigidity given by the strain orientation entropy should be proportional to the concentration and to the absolute

temperature.[14] We shall tentatively assign the value calculated from Eq. 6, which has the proper concentration dependence, and depends only slightly upon the temperature (measurements are not sufficiently accurate to establish the theoretical relationship), as the contribution of orientation entropy to the rigidity. It amounts to 20% of the rigidity of the 15% solution, and less at higher concentrations.

Relation between Viscosity and Rigidity.— The Maxwell function[15] for the relaxation of stress at constant strain, $\mathfrak{T} = \mathfrak{T}_0 e^{-t/\tau}$, is derived from the differential equation

$$\frac{d\gamma}{dt} = \frac{1}{G}\left(\frac{d\mathfrak{T}}{dt} + \frac{\mathfrak{T}}{\tau}\right) \qquad (7)$$

and this describes the rate of strain at constant stress as $\mathfrak{T}/G\tau$, thereby identifying the viscosity coefficient with $G\tau$.

Kuhn,[16] and Bennewitz and Rötger,[17] showed that if a system contained several different internal mechanisms for maintaining shearing stress, each associated with its contribution to the modulus of rigidity, G_i, and each undergoing Maxwell relaxation characterized by a time τ_i, then the total rigidity should be $\Sigma_i G_i$ and the viscosity $\Sigma_i G_i \tau_i$. If, however, the duration of an experimental measurement of rigidity should be short compared with some of the times τ_i, and long compared with the others, only the rigidities corresponding to the first group would be detected, and the remainder would be lost.

In applying this concept to the system polystyrene–xylene, we shall limit ourselves to two mechanisms, and write

$$\eta = G_1\tau_1 + G_2\tau_2 \qquad (8)$$

The preceding discussion of anomalous viscosity and elastic recoil shows that there is one contribution to rigidity which is proportional to the concentration and of the order of 10^4 dyne cm.$^{-2}$. We employ this in the first term of (8) and set $G_1 = G' = G_a$. The associated relaxation time, τ_1, must be of the order of seconds, at high concentrations; otherwise the elastic recoil could not be detected in an experimental measurement which is of comparatively long duration. The form of the recoil function shows that there is not a single time associated with G_1, but a broad distribution

(13) Eisenschitz [*Kolloid Z.*, **64**, 184 (1933)] following the hydrodynamics of Hencky [*Ann. Physik*. [5] **2**, 617 (1929)]. deduced a function of the form $\eta' = \eta/(1 + \mathfrak{T}^2/G^2)$. It does not, however, fit our data on polystyrene solutions.

(14) *Cf.* Kuhn, (a) *Kolloid Z.*, **76**, 258 (1936): (b) **87**, 3 (1939).

(15) Maxwell, *Phil. Trans. Roy. Soc.*, **157**, 52 (1867); see Eq. (3) of the previous paper.[1]

(16) Kuhn, *Z. physik. Chem.*, **B42**, 1 (1939).

(17) Bennewitz and Rötger, *Physik. Z.*, **40**, 416 (1939).

of them; as a first approximation, however, we shall consider a single mean time, τ_1.

The high frequency rigidity as determined by propagation of transverse vibrations,[1] G^0, may be assumed to represent the total rigidity, $G_1 + G_2$. The second modulus, therefore, is given by $G_2 = G^0 - G_1$. And the relaxation time associated with this contribution, τ_2, has been estimated from the dispersion and damping as 4×10^{-4} sec., sensibly independent of concentration.

Since the viscosity has been measured, the only unknown in Eq. 8 is τ_1, and this may be calculated by substitution of the known parameters, as in Table VI.

TABLE VI

ANALYSIS OF RIGIDITY MECHANISMS, AT 25°

Concn. poly-styrene, %	$G^0 \times 10^{-4}$	$G_1 \times 10^{-4}$	$G_2 \times 10^{-4}$	η	$\tau_2 \times 10^4$	$\tau_1 \times 10^2$	$\tau_1/\eta \times 10^4$
15	0.75	0.16	0.59	13.1	4.0	0.73	5.6
20	1.66	.22	1.44	52.5	4.0	2.12	4.0
25	2.82	.28	2.54	209	4.0	7.1	3.4
30	4.80	.33	4.47	660	4.0	19.5	3.0
35	9.34	.39	8.95	2,000	4.0	50	2.5
52.3	380	1.2	379	116,000	4.0	950	0.8

According to this analysis, mechanism 1 is associated with a modulus of rigidity which is proportional to the concentration (up to 30%), of the order of 10^4 dyne cm.$^{-2}$, and a mean relaxation time which varies markedly with concentration and is roughly proportional to the macroscopic viscosity.[18] Mechanism 2 is associated with a modulus of rigidity which varies markedly with concentration, and a relaxation time independent of concentration. Mechanism 2 contributes most of the rigidity, but mechanism 1 contributes most of the viscosity. In a state of constant stress (steady flow), the internal strain associated with mechanism 1 is much greater than that associated with mechanism 2, because of the difference in rigidities.[19]

The elastic recoil is readily explained on this basis. When the load is removed, mechanism 2 relaxes almost immediately, leaving the internal

(18) There are two molecular relaxation mechanisms for which τ has been calculated to be proportional to the viscosity, and, although neither of them has any probable significance in the present case, it may be of interest to substitute our value of τ/η in the respective formulas. Stokes rotation of a sphere (Debye, "Polar Molecules," Chemical Catalog Co., New York, N. Y., 1929) would require for the molecular volume a value of 3×10^8; this, however, is obviously without significance. Rotatory diffusion of a long chain polymer as calculated by Kirkwood and Fuoss [*J. Chem. Phys.*, **9**, 329 (1941)] would require a degree of polymerization of 3×10^5; the actual value quoted by the manufacturer is 1.1×10^3.

(19) This reasoning may be illustrated by a mechanical model consisting of two units in parallel, each unit made up of a spring with an elastic force G_i, in series with a piston with a viscous force of $G_i \tau_i$. The extension of each spring is the corresponding γ_i.

strain associated with mechanism 1 to be relieved by a slower process. According to the theory of Kuhn, the time characterizing this process is $\tau_2 G_2 / G_1$, which is, for our 52.3% solution, 0.13 sec. However, the temperature dependence of the observed mean recoil time, which is close to that of the macroscopic viscosity, suggests that it might better be represented simply by τ_1. The magnitude of the latter, 9.5 sec., is also closer to the observed recoil time at 25°, which is 38 sec. Some discrepancy may be expected owing to the approximation of taking a single mean time instead of a distribution of time constants.

Although τ_1 is a mean value of a fairly wide distribution of relaxation times, as shown by the form of the recoil function (Fig. 6), nevertheless τ_2 appears to be a rather sharply defined time constant, so that the distribution of times in its neighborhood, if any, is narrow. This is indicated by the dispersion of velocity of transverse vibrations (Fig. 3 of the previous paper), which can be described within experimental error by a single relaxation time. It is not clear, of course, whether there is actually a gap in the distribution of times between the wide peak at τ_1 and the narrow peak at τ_2, or whether a continuous distribution of relaxation times extends over this interval.

Identification of Mechanisms with Molecular Processes.—Mechanism 1 has already been postulated to be the uncurling of flexible molecules. The magnitude of τ_1 and its marked dependence upon concentration indicates that the relaxation process involves much interference between neighboring polymer molecules, which would be expected if long segments of the chains are aligned or oriented.

The nature of mechanism 2 is less clearly indicated, but it may be tentatively discussed. In the preceding paper, it was postulated that if a part of the rigidity is due to orientation entropy, the remainder may be due to transfer of stress by intermolecular forces. It seems unlikely that van der Waals forces of attraction could support stress with a relaxation time as large as 10^{-4} sec. The support is more probably achieved through repulsive forces, at points where the chain molecules are entangled and cannot move past each other. In a molecule thus caught and immobilized strain could occur through the bending and stretching of valence bonds along the chain. From the force constants for organic molecules

deduced from Raman spectra,[20] it is clear that considerably more force is required to stretch a carbon–carbon bond than to bend the $C{\diagup}^{C}{\diagdown}_C$ angle, and that most of the deformation should come from the latter source. The rigidity should increase with the number of "points of entanglement" where chains cross (which increases with concentration, more rapidly than the first power), and with diminishing distance between points of entanglement. Thus the rigidity may be expected to vary with a fairly high power of the concentration. Empirically we find that G_2 is proportional to the third power, as Fig. 8 shows

$$G_2 = 1.3 \times 10^6 \, c^3 \text{ dyne cm.}^{-2} \qquad (9)$$

where c is expressed in g./cc. It may be possible to derive from statistics a relation corresponding to (9) and to relate the empirical constant to the bending constant for the carbon bond angle.
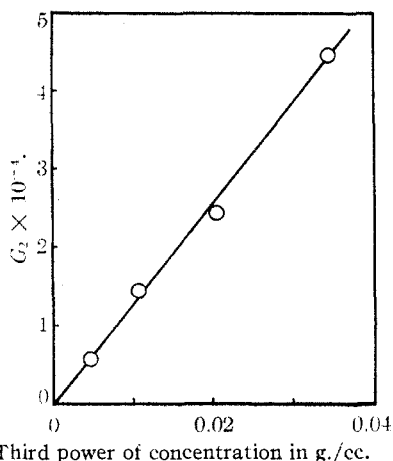

Fig. 8.—Modulus of rigidity of the second mechanism, G_2, plotted against the third power of the concentration expressed as g./cc.

It is perhaps reasonable that the relaxation of stress from such a repulsion effect should be independent of concentration, as has been found for τ_2. The lack of variation of τ_2 with temperature, however, remains unexplained. According to the concept of Eyring,[21] a molecular process with a relaxation time of this magnitude should be associated either with an energy of about 12 kcal., and accordingly be strongly temperature dependent, or else with a very large entropy effect.

In concluding, it may be pointed out that the interpretation of mechanical properties in terms of the behavior of molecules of known structure, such as polystyrene, may facilitate the study of more complicated systems, such as polysaccharides and proteins, in which less is known of the structure, and in which a greater variety of intermolecular forces is involved.

Summary

1. The viscosities of solutions of polystyrene in xylene have been studied over a concentration range of 15.4 to 52.3% and a temperature range of 1° to 30°.

2. The dependence of viscosity upon shearing stress can be described by a single parameter which is proportional to concentration up to 30% and is interpreted as an internal modulus of rigidity.

3. The dependence of viscosity upon temperature follows the usual exponential relation and is associated with activation energies ranging from 3.8 to 10.7 kcal.

4. The dependence of viscosity upon concentration shows positive deviation from a linear logarithmic plot, and can be described by the theory of Powell, Clark and Eyring.

5. The elastic recoil at 52.3% concentration is described by a modulus of rigidity identical with that characterizing the dependence of viscosity upon shearing stress, and a relaxation function whose mean time constant varies with temperature in the manner of a viscosity with an activation energy of 9.3 kcal.

6. The viscosity and rigidity data are all interpreted in terms of two molecular mechanisms, each with a characteristic modulus of rigidity and relaxation function. One of these, in which the modulus of rigidity is proportional to concentration (up to 30%), and the mean relaxation time approximately proportional to the macroscopic viscosity, is tentatively identified with the uncurling of flexible chain molecules. The other, in which the modulus of rigidity is proportional to the third power of the concentration (up to 30%), and the relaxation time is independent of concentration (and hence viscosity), is tentatively identified with the bending of carbon–carbon bonds.

(20) Kohlrausch. "Der Smekal-Raman Effekt." Ergänzungsband, J. Springer, Berlin, 1938, p. 132.

(21) Eyring, J. Chem. Phys., 4, 283 (1936); Kauzmann and Eyring, THIS JOURNAL, 62, 3113 (1940).