

isolated by filtering, washing with water and then acetone, and drying, was shown to be 2-amino-4-hydroxypteridine-6-carboxylic acid (III) by comparison of the ultraviolet absorption curve with that of an authentic sample.<sup>3</sup>

**9,10-Dimethylpteroic Acid (IV).**—This was prepared similarly to V above, except that *p*-methylaminobenzoic acid<sup>5</sup> was used (see Table I for ultraviolet absorption and biological data).

*Anal.* Calcd. for  $C_{16}H_{16}N_6O_3 \cdot 0.5H_2O$ : C, 55.1; H, 4.91; N, 24.1. Found: C, 54.7; H, 4.99; N, 24.0.

**N-[N-[1-(2,4-Diamino-6-pteridyl)-ethyl]-N-methyl-amino]-benzoyl]-glutamic Acid, ("4-Amino-9,10-dimethylpteroylglutamic Acid") (VI).**—This compound was prepared by the method of Waller, *et al.*,<sup>1</sup> using 2,4,5,6-tetraminopyrimidine sulfate,<sup>9</sup> 2,2,3-trichlorobutyraldehyde and *p*-methylaminobenzoylglutamic acid.<sup>5</sup> A mixture of 31.6 g. of the crude, 9 g. of lime, and 2 l. of water was heated at 60° for forty minutes. After filtration, the cake was washed with 600 ml. of water at 60°. The combined filtrate and wash liquors were adjusted to pH 10.8–11.0 with 10% aqueous zinc chloride. The mixture was filtered, and the filtrate was adjusted to pH 3.5–4.0 with hydrochloric acid. After cooling to 5°, the precipitate was filtered, washed with water and slurried in 1500 ml. of water containing sodium hydroxide to give pH 11–11.5. After heating it at 60° for ten minutes, the pH of the solution was reduced to 7, while cooling the mixture to 20°, and filtered. The filtrate was adjusted to pH 3.5–4.0 with hydrochloric acid and cooled to 5°. After filtration, the cake was slurried in 1 l. of water containing enough lime to obtain pH 8.5–9 at 60° and filtered hot with 1.5 g. of char-

coal. The filtrate was adjusted to pH 3.5–4.0 with hydrochloric acid and cooled to 0–5° overnight. The yellow-orange microcrystalline material which separated was isolated by filtration and was analytically pure. The biological and ultraviolet absorption data are shown in Table I.

*Anal.* Calcd. for  $C_{21}H_{24}N_8O_5 \cdot 2H_2O$ : C, 50.0; H, 5.55; N, 22.2. Found: C, 50.4; H, 5.42; N, 21.5.

**Acknowledgment.**—We are indebted to Mr. Richard L. Shepard for technical assistance in the preparation of certain of these substances, to Miss Ruth Abbott for the ultraviolet absorption data, and to Mr. O. Sundberg and co-workers for the microanalyses.

### Summary

N-[4-{[1-(2-Amino-4-hydroxy-6-pteridyl)-ethyl]-amino}-benzoyl]-glutamic acid (II), designated herein as 9-methylpteroylglutamic acid, has been synthesized and isolated in pure form. Corresponding analogs which have also been prepared are 9,10-dimethylpteroylglutamic acid (V), 4-amino-9,10-dimethylpteroylglutamic acid (VI), and 9,10-dimethylpteroic acid (IV).

These compounds exhibit antagonism for pteroylglutamic acid in the growth of *S. faecalis* R.

BOUND BROOK, NEW JERSEY

RECEIVED SEPTEMBER 27, 1948

(9) Traube, *Ber.*, **37**, 4545 (1904).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

## Mechanical Properties of Substances of High Molecular Weight. V. Rigidities of Polyisobutylene Solutions in Various Solvents<sup>1</sup>

BY J. N. ASHWORTH<sup>2</sup> AND JOHN D. FERRY

Many concentrated solutions of linear polymers behave as highly viscous liquids in steady flow, but possess solid-like rigidity in small oscillating deformations; transverse waves can be propagated in them at audio frequencies. From the wave length of these waves the rigidity can be calculated, and from the damping the mechanical loss, or the dynamic viscosity, can be derived. Measurements of this sort on solutions of polystyrene in xylene have been reported previously.<sup>3</sup>

In seeking to understand the mechanism of rigidity in polymer solutions, it is desirable to study a variety of molecular types. In this paper, measurements are reported for a non-polar polymer for which complications due to intermolecular forces should be at a minimum: polyisobutylene. As in the earlier work on polystyrene, the dependence of rigidity on frequency, concentration, and temperature has been studied. Also, four different solvents have been employed.

(1) Supported in part by the Research Committee of the Graduate School of the University of Wisconsin from funds supplied by the Wisconsin Alumni Research Foundation, and in part by a grant from Research Corporation.

(2) Present address: Rohm and Haas Co., Philadelphia, Pa.

(3) J. D. Ferry, *THIS JOURNAL*, **64**, 1323 (1942).

### Materials

The polyisobutylene was kindly furnished by Dr. John Rehner, Jr., of the Esso Laboratories. It was designated 303-92-1. From measurements of viscosities of dilute solutions in di-isobutylene, the intrinsic viscosity in this solvent at 20° was found to be 2.85 (g./100 cc.)<sup>-1</sup>, corresponding to a viscosity-average molecular weight of 1,200,000 on the basis of the interpolation equation of Flory.<sup>4</sup> Intrinsic viscosities in the solvents used for the rigidity studies were also determined at 20° and 30°; these are given in Table IV below. The details of the intrinsic viscosity measurements are presented elsewhere.<sup>5</sup>

In most cases, the polymer was used without purification. However, it contained a small amount of tiny fibrous foreign particles which, though negligible in quantity, were optically anisotropic and interfered somewhat with optical measurements of waves. Accordingly, a portion of the polymer was dissolved in toluene at a concentration of about five per cent., clarified by filtration through Whatman No. 4 filter paper on a

(4) P. J. Flory, *ibid.*, **65**, 372 (1943).

(5) J. N. Ashworth, Ph.D. Thesis, University of Wisconsin, 1948.

Buchner funnel, completely precipitated by methyl alcohol, and dried *in vacuo* at room temperature for twelve hours and at 60° for four hours. This preparation, hereafter referred to as clarified polymer, afforded the best measurements of damping.

The *n*-heptane was "99 mole per cent." sold by the Phillips Petroleum Corp. Xylene was obtained from Mallinckrodt and Merck, and chlorobenzene and isoöctane (2,2,4-trimethylpentane) from the Eastman Kodak Company. The solvents were used without further purification.

Preparation of concentrated solutions was expedited by rotating bottles containing polymer and solvent at about 12 revolutions per hour. Concentrations were determined by dry weight after heating samples *in vacuo* for twenty-four hours at 110°. Concentrations were expressed both as weight per cent. and as g./cc. The latter values were calculated assuming additivity of the volumes of polymer and solvent, taking the density of polymer as 0.91 and those of the solvents from the "International Critical Tables," and assuming that the thermal expansion coefficients of solutions were the same as those of the respective solvents.<sup>3</sup>

### Method

The apparatus and procedure were the same as previously described,<sup>3,6</sup> with some minor modifications. The Strobotron was mounted outside the air thermostat, and its illumination of the cell was improved by a reflector and a condensing lens. Photographic recording of the wave pattern was substituted for the former method of visual observation with horizontal and vertical micrometer adjustments. The rather faint pattern was satisfactorily photographed on Eastman Kodak Co. CTC plates or Contrast Process Panchromatic cut film, the latter affording a contrast between light and dark Babinet bands which was an improvement over visual observation.

The photographs of wave patterns were projected by an enlarger on cross-section paper, and the contours of the wavy Babinet bands were traced in pencil. An example is shown in Fig. 1. Similar projections of photographs of the undeviated Babinet bands, when superimposed, permitted measurements of the displacements from which damping data were calculated. The wave length was taken as the average of ten or more measured distances between successive maxima or minima on each photograph. There was no perceptible change in wave length with distance from the vibration source.

As in the previous studies on polystyrene, the damping was within experimental error exponential; a plot of  $\ln \delta$  ( $\delta$  being the double refraction in the solution observed at the maxima and minima of the stroboscopically immobilized wave) against  $x$ , the distance from the vibrator plate, was a

(6) J. D. Ferry, *Rev. Sci. Instruments*, **12**, 79 (1941).

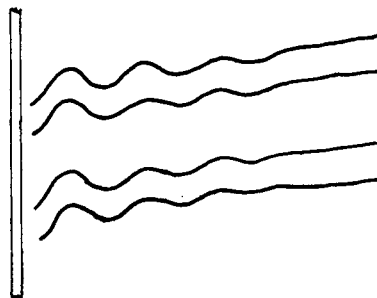


Fig. 1.—Tracing of wave pattern in 15.7% polyisobutylene in chlorobenzene, 17.1°, 400 cycles/sec. The vibrator plate is indicated at left.

straight line.<sup>7</sup> The reciprocal slope of the line is  $x_0$ , the critical damping distance. Values of  $\delta$  can be calculated from the equation<sup>6</sup>  $\tan \delta = \tan \Delta \sin 2\alpha$ , where  $\Delta$  is the relative retardation corresponding the Babinet line displacement, and  $\alpha$  is the angle between the axes of the Babinet and the polarizer. However, a simpler procedure was followed; since  $\sin 2\alpha$  is small (in our case  $\alpha = 2^\circ 14'$ ),  $\tan \delta$  is nearly equal to  $\delta$ , and  $\tan \Delta$  is proportional to  $\delta$ ; it follows that the reciprocal slope of a plot of  $\ln \tan \Delta$  against  $x$  is  $x_0$ , and the critical damping distance is obtained without calculating  $\delta$  directly.

The wave rigidity,<sup>1</sup>  $\tilde{G}$ , was calculated as  $\lambda^2 \nu^2 \rho$ , where  $\lambda$  is the measured wave length,  $\nu$  the frequency, and  $\rho$  the density. The latter value was calculated assuming additivity of the volumes of polymer and solvent. The dimensionless damping index,<sup>9</sup>  $\lambda/x_0$ , was used to characterize the severity of the damping.

Different sizes of cells and vibrator plates were used in four combinations (Fig. 2). Comparisons of the same solutions with different cells and plates

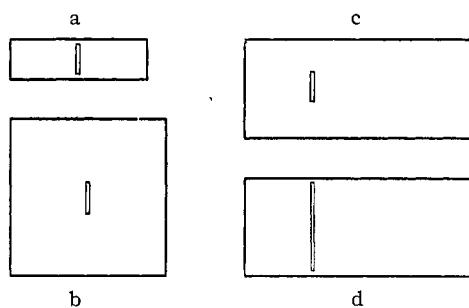


Fig. 2.—Cell-plate combinations (top view). Cell sizes: a, 1.0 × 3.5 cm.; b, 4.0 × 4.0 cm.; c and d, 2.5 × 6.0 cm. Plate widths: a, b, and c, 0.8 cm.; d, 2.5 cm.

(7) The first maximum or minimum often deviated materially. This is to be expected from theoretical calculations<sup>8</sup> of wave propagation in which the finite dimensions of the cell are taken into account. The calculations show that the value of  $x_0$  determined as outlined here is within a few per cent., and hence well within experimental error, of the value which would characterize the damping of a plane wave in a medium of infinite extent.<sup>9</sup>

(8) F. T. Adler, W. M. Sawyer and J. D. Ferry, unpublished work.

(9) J. D. Ferry, W. M. Sawyer and J. N. Ashworth, *J. Polymer Sci.*, **2**, 593 (1947).

revealed no differences in  $\bar{G}$  and  $\lambda/x_0$  exceeding experimental scatter. Most measurements were made with combinations (c) and (d), which provided room for longer wave trains. The widest frequency range was achieved with combination (d). The cell used in (c) and (d) was of aluminum with glass windows cemented with litharge and glycerol.

In some cases the dynamic rigidity  $G'$  and the dynamic viscosity  $\eta'$ , which are useful for comparison with results of other experimental methods and for theoretical interpretation, were calculated by the equations<sup>9</sup>

$$G' = \bar{G} \frac{4\pi^2[4\pi^2 - (\lambda/x_0)^2]}{[4\pi^2 + (\lambda/x_0)^2]^2} \quad (1)$$

$$\eta' = \frac{\bar{G}}{\omega} \frac{16\pi^3\lambda/x_0}{[4\pi^2 + (\lambda/x_0)^2]^2} \quad (2)$$

where  $\omega$  is  $2\pi$  times the frequency.

### Results

**Dispersion of Rigidity.**—In experiments where a frequency range of five or sixfold was achieved, a small increase in  $\bar{G}$  with increasing frequency was observed. Representative data for clarified polymer in chlorobenzene solutions are given in Table I (concentrations expressed in weight per cent). The dependence of  $\bar{G}$  on the frequency can be approximated by straight lines of equal slope (Fig. 3).

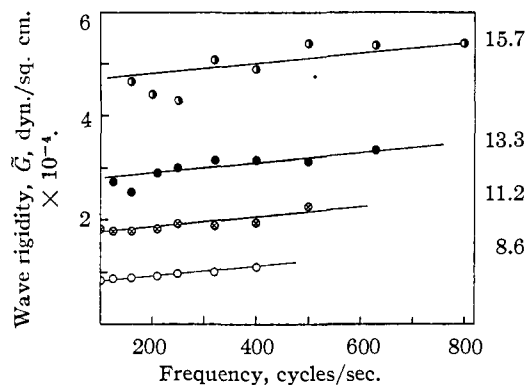


Fig. 3.— $\bar{G}$  plotted against frequency for chlorobenzene solutions at 25°. Figures opposite the lines denote concentrations in weight per cent.

In other experiments, where the frequency range was limited to three or fourfold, the dispersion of  $\bar{G}$  was within experimental scatter (5 to 10%). It was, in any case, so small that the dispersion function appears to be essentially a plateau in the range from 100 to 1000 cycles/sec. for our solutions. Accordingly, to determine the dependence of  $\bar{G}$  on concentration and temperature, values measured at different frequencies were simply averaged.

**Dependence of Rigidity on Concentration and Temperature.**—Average values of  $\bar{G}$ , together with the frequency range covered in each

TABLE I  
DISPERSION OF  $\bar{G}$  IN CHLOROBENZENE SOLUTIONS AT 25°

Frequency, cycles/sec.	$\bar{G}$ , dyn./sq. cm., $\times 10^{-4}$ Concn. =			
	8.6%	11.2%	13.3%	15.7%
100	..	1.82	..	..
110	0.85	..	..	..
125	.88	1.80	2.73	..
160	.89	1.80	2.54	4.67
200	..	..	..	4.38
210	.96	1.83	2.90	..
250	.99	1.93	3.00	4.31
320	1.00	1.89	3.15	5.11
400	1.12	1.93	3.16	4.90
500	..	2.24	3.13	5.39
630	..	..	3.36	5.34
800	..	..	..	5.41

case, are given for solutions in *n*-heptane at different concentrations and temperatures in Table II. At constant weight concentration, the rigidity decreases somewhat with increasing temperature,

TABLE II  
 $\bar{G}$  OF *n*-HEPTANE SOLUTIONS

Concn. polymer, %	Frequency range, cycles/sec.	Temp., °C.	$\rho$ , g./cc.	$\bar{G}$ , dyn./ sq. cm., $\times 10^{-4}$	$\bar{G}/\rho^2$ $\times 10^{-8}$
13.1	125-320	-6.9	0.0955	0.66	7.5
		1.3	.0946	.62	7.3
		10.5	.0935	.59	7.2
		18.5	.0926	.57	7.2
		28.4	.0916	.57	7.4
		35.2	.0908	.51	6.8
Av.					7.2
15.4	160-400	1.0	0.112	1.12	8.0
		10.9	.111	1.05	7.7
		18.8	.110	1.12	8.4
		27.5	.109	1.06	8.2
		35.4	.108	1.00	8.0
Av.					8.1
20.1	125-500	-7.8	0.149	2.88	8.7
		0.9	.148	2.82	8.7
		10.9	.146	2.59	8.4
		19.3	.145	2.98	9.7
		27.8	.143	2.59	8.7
		34.6	.144	2.50	8.7
Av.					8.8
25.0	125-630	-5.0	0.188	5.56	8.4
		1.3	.187	5.48	8.4
		11.1	.185	5.49	8.8
		19.5	.183	5.33	8.8
		28.4	.181	5.09	8.6
		36.5	.179	4.88	8.6
Av.					8.6
29.7	160-800	-6.0	0.226	9.01	7.8
		1.4	.224	8.98	7.9
		10.9	.221	8.23	7.6
		18.9	.219	8.41	8.0
		28.3	.217	7.91	7.7
Av.					7.8
Over-all average					8.1

about 0.3% per degree. In the case of polystyrene-xylene solutions, where a somewhat more pronounced decrease was observed,<sup>3</sup> the temperature dependence of  $\bar{G}$  could be described by the relation  $\bar{G} = A_G e^{Q_G/RT}$ , with  $Q_G = 1500$  cal. The results of Table II can also be fitted by this relation, with  $Q_G = 550$  cal. However, for polyisobutylene, the temperature dependence at constant weight concentration can be entirely attributed to the change in volume concentration due to thermal expansion; when rigidities are compared at constant *volume* concentration, the temperature dependence vanishes.

Proportionality of  $\bar{G}$  to the third power of  $c$ , the volume concentration (g./cc.) was anticipated from the behavior of polystyrene.<sup>10</sup> The last column of Table II shows that for polyisobutylene in *n*-heptane  $\bar{G}/c^3$  is constant for each solution over a temperature range from about  $-7$  to  $35^\circ$ . The average values of  $\bar{G}/c^3$  for each solution are also close together, and no trend with increasing concentration is apparent.<sup>12</sup>

TABLE III

VALUES OF  $\bar{G}/c^3$  FOR SOLUTIONS IN XYLENE, ISOÖCTANE, AND CHLOROBENZENE

Solvent	Concn., wt. %	$\bar{G}/c^3 \times 10^{-4}$	Av.
Xylene	10.3 <sup>c</sup>	8.9	9.4
	11.5 <sup>a</sup>	9.3	
	11.5 <sup>b</sup>	9.7	
	15.3 <sup>a</sup>	9.6	
	15.3 <sup>c</sup>	9.6	
	18.5 <sup>c</sup>	8.9	
	18.7 <sup>ae</sup>	11.1	
	18.7 <sup>ca</sup>	9.7	
	18.7 <sup>de</sup>	11.1	
	24.5 <sup>c</sup>	8.6	
	25.1 <sup>ca</sup>	9.1	
Isoöctane	25.3 <sup>a</sup>	9.5	10.1
	28.7 <sup>c</sup>	7.9	
	33.5 <sup>c</sup>	7.9	
	10.7 <sup>df</sup>	12.2	
	15.4 <sup>c</sup>	9.0	
	19.7 <sup>d</sup>	10.2	
Chlorobenzene	26.4 <sup>df</sup>	9.1	10.9
	8.6 <sup>def</sup>	11.9	
	11.2 <sup>def</sup>	10.8	
	13.3 <sup>def</sup>	10.2	
	15.7 <sup>de</sup>	10.5	

<sup>a</sup> Cell-plate combination a. <sup>b</sup> Cell-plate combination b.

<sup>c</sup> Cell-plate combination c. <sup>d</sup> Cell-plate combination d.

<sup>e</sup> Clarified polymer. <sup>f</sup> Measured at  $25^\circ$  only.

(10) Proportionality to  $c^3$  was shown for the rigidity of polystyrene solutions after a calculated low-frequency component of rigidity had been subtracted from the measured values.<sup>11</sup> However, the low-frequency component was so small that the relation holds also for the total rigidity (see Fig. 7).

(11) J. D. Ferry, *THIS JOURNAL*, **64**, 1330 (1942).

(12) Since the frequency range represented by the average  $\bar{G}$  changes somewhat with concentration (Table II), this does not quite represent a test of the third power relation at constant frequency. Values interpolated from Fig. 3 at constant frequency and plotted logarithmically against  $\log c$  give slopes ranging from 2.7 to 3.0. However, these small differences are too close to experimental error to attempt to describe at present.

Data for the other solvents are given in detail in the thesis<sup>5</sup> on which this paper is based. In each case  $\bar{G}$  decreased about 0.3% per degree at constant weight concentration, but  $\bar{G}/c^3$  was independent of temperature and concentration.<sup>13</sup> The values of  $\bar{G}/c^3$  averaged at different temperatures for each solution are given in Table III.

In Table IV, the over-all averages of  $\bar{G}/c^3$  for the four solvents are correlated with the respective intrinsic viscosities at 20 and  $30^\circ$ . The intrinsic viscosities show that the solvents are arranged in the order of decreasing solvent power; the temperature dependence, which is probably significant only for chlorobenzene, also indicates that this is a somewhat poorer solvent than the others. The differences are on the whole slight, but it is clear that the order of decreasing intrinsic viscosity is the order of increasing rigidity.

TABLE IV

AVERAGE VALUES OF  $\bar{G}/c^3$  AND INTRINSIC VISCOSITIES

Solvent	$\bar{G}/c^3$ , (dyn./sq. cm.) (g./cc.) <sup>-3</sup> $\times 10^{-6}$	$[\eta]$ , $20^\circ$	$[\eta]$ , $30^\circ$
	<i>n</i> -Heptane	8.1	2.68
Xylene	9.4	2.63	2.67
Isoöctane	10.1	2.45	2.36
Chlorobenzene	10.9	2.15	2.35

**Damping.**—In almost all cases, the damping index,  $\lambda/x_0$ , varied within the rather narrow range from 0.6 to 1.2. Except in a few cases, the experimental scatter did not permit a reliable study of the dependence of damping index on concentration, temperature, or nature of solvent; as a first approximation, it was independent of all these variables.

With increasing frequency,  $\lambda/x_0$  generally decreased. The best measurements, on chlorobenzene solutions, are given in Table V and plotted against the logarithm of the frequency in Fig. 4.

**Dynamic Rigidity and Viscosity.**—From the data in Tables I and V, the dynamic rigidity  $G'$  and the dynamic viscosity  $\eta'$  of the chlorobenzene

TABLE V

DAMPING INDICES IN CHLOROBENZENE AT  $25^\circ$

Frequency, cycles/sec.	Damping index, $\lambda/x_0$ Concn. =		
	11.2%	13.3%	15.7%
125	1.14	..	..
160	0.97	..	..
200	..	..	1.20
210	1.00	0.96	..
250	0.79	.96	0.86
320	.77	.72	.94
400	.64	.69	.55
500	.73	.66	.82
630	..	.70	.74
800	..	..	.64

(13) Since the thermal expansion coefficients of the solvents are all very nearly one-tenth per cent. per degree,  $c^3$  decreases three-tenths per cent. per degree, accounting exactly for the observed decrease in rigidity.

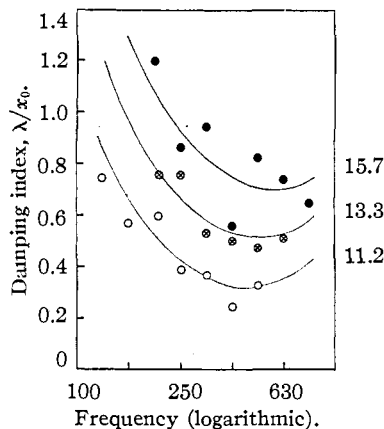


Fig. 4.—Damping indices for chlorobenzene solutions, plotted against the logarithm of the frequency. Figures opposite the curves denote concentrations in weight per cent. The ordinate scale refers to the 15.7% curve; the curves for 13.3% and 11.2% have been shifted downward 0.2 and 0.4 unit, respectively. The curves are calculated for retarded Maxwell elements, using the constants of Table VI.

solutions were calculated by equations (1) and (2), and they are plotted against the logarithm of the frequency in Figs. 5 and 6. The rigidity  $G'$  is from three to ten per cent. smaller than  $\bar{G}$ . The viscosity  $\eta'$  is of the order of a few poises and falls off rapidly with increasing frequency; this is the usual behavior found for concentrated polymer solutions by direct measurements with transducer methods.<sup>14</sup> By contrast, the viscosity in steady flow of these solutions is of the order of hundreds to thousands of poises.

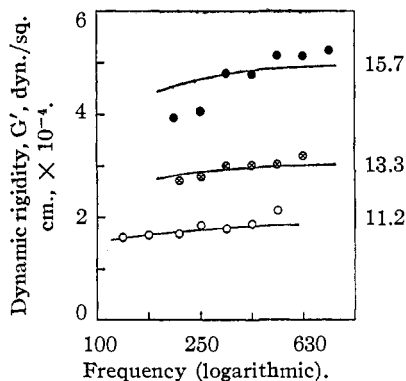


Fig. 5.—Dynamic rigidities of chlorobenzene solutions, plotted against the logarithm of the frequency. Figures opposite the curves denote concentrations in weight per cent. The curves are calculated for retarded Maxwell elements, using the constants of Table VI.

Since  $G'$  never differs from  $\bar{G}$  by more than 10% in our experiments, the two rigidities can be taken as equivalent for some purposes, as in Fig. 7,

(14) T. L. Smith, J. D. Ferry and F. W. Schremp, *J. Appl. Physics*, in press.

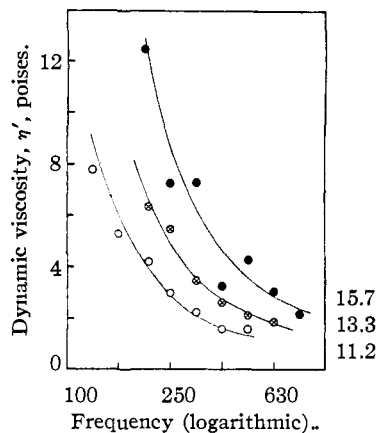


Fig. 6.—Dynamic viscosities of chlorobenzene solutions, plotted against the logarithm of the frequency. Figures opposite the curves denote concentrations in weight per cent. The curves are calculated for retarded Maxwell elements, using the constants of Table VI.

where  $\bar{G}$  values for solutions are compared with  $G'$  for the undiluted polymer. In most cases the accuracy of  $\lambda/x_0$  is insufficient for an adequate calculation of  $\eta'$ , although its order of magnitude can always be estimated from Eq. 2, since  $\lambda/x_0$  almost never exceeds the range 0.6–1.2.

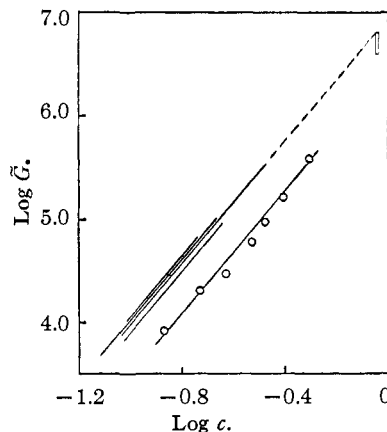


Fig. 7.— $\text{Log } \bar{G}$  plotted against  $\text{log } c$ . Solid lines (drawn with slope of 3), in descending order: polyisobutylene in chlorobenzene, isoöctane, xylene, and heptane; polystyrene in xylene (points from ref. 3). Rectangle:  $G'$  of pure polyisobutylene (ref. 16).

## Discussion

**Representation of Frequency Dependence by a Mechanical Model.**—A simple model which can imitate approximately the frequency dependence of mechanical properties of concentrated polymer solutions in the audio frequency range is a retarded Maxwell element,<sup>9</sup> with a viscous dashpot ( $\eta_S$ ) in series with a parallel combination of spring ( $G$ ) and dashpot ( $\eta_P$ ). The three model constants are frequency-independent. In the range where  $\omega\eta_S/G \sim 10$ , when  $\eta_P \ll \eta_S$ , the

model gives the following dispersion behavior: both  $\bar{G}$  and  $G'$  are represented by plateaus, almost equal to  $G$ , with a drop at lower frequencies, while the former rises at higher frequencies;  $\eta'$  decreases with increasing frequency; and  $\lambda/x_0$  goes through a minimum. The equations are given elsewhere,<sup>9,15</sup> together with illustrative graphs.

This behavior is qualitatively similar to the experimental dispersion shown in Figs. 3-6; and, for these chlorobenzene solutions, a fairly good quantitative fit is obtained, taking  $\eta_P/\eta_S = 0.013$ . The model constants chosen are given in Table VI, and the calculated curves are drawn in Figs. 4-6.

As would be expected from the fact that  $G \cong G' \cong \bar{G}$  in this frequency range, the frequency-independent rigidity  $G$  is proportional to  $c^3$ . Both viscosities are proportional to  $c^2$  in this case, so that the two relaxation times,  $\tau_S = \eta_S/G$  and  $\tau_P = \eta_P/G$ , are inversely proportional to  $c$ . It should be noted that  $\eta_S$  is smaller than the steady flow viscosity by a factor of about 0.03, so the utility of the model does not extend to zero frequency.

For most of the other solutions, experimental scatter does not permit model fitting. However, from the magnitudes of  $\lambda/x_0$ , it is clear that any application of a retarded Maxwell element would be restricted to  $\eta_P/\eta_S$  ratios of the order of 0.01. For the xylene solutions,  $\tau_S$  appeared to increase with increasing concentration.

TABLE VI

CONSTANTS OF RETARDED MAXWELL ELEMENTS DESCRIBING DISPERSION IN CHLOROBENZENE SOLUTIONS AT 25°

Concn., g./cc.	$G \times 10^{-4}$ , dyn/ sq. cm.	$\eta_S$ poise	$\eta_P$ poise	$G/c^3$ $\times 10^{-6}$	$\tau_S/c^2$ $\times 10^{-3}$
0.120	1.9	61	0.79	10.9	4.1
.143	3.1	90	1.1	10.6	4.3
.167	5.1	128	1.6	10.9	4.5

It is evident that important frequency-dependent phenomena must exist at lower frequencies than those employed here, since the rigidity must drop from the plateau exhibited in our frequency range to zero under constant stress.

**Dependence of Rigidity on Concentration.**—Pending measurements of dynamic rigidity at higher concentrations, which will require a different experimental method, it is of interest to extrapolate the  $c^3$  relation to the pure polymer ( $c = 0.91$  g./cc.). Of course, the four solvents do not extrapolate into the same point, but the differences are small, as shown in Fig. 7; the value obtained is about  $6 \times 10^6$  dyn./sq. cm. at 25°. This agrees quite well with measurements of  $G'$  on the same sample of polymer by a twin transducer method,<sup>16</sup> which gave a range from 4 to  $6 \times 10^6$  in the frequency range from 50 to 250 cycles/sec.

(15) J. D. Ferry, *J. Res. Nat. Bureau Standards*, **41**, 53 (1948).

(16) R. S. Marvin, E. R. Fitzgerald and J. D. Ferry, reported at the Los Angeles meeting of the Rubber Division of the American Chemical Society, July 22, 1948.

As a first approximation, apparently, all the solutions can be regarded as dilutions of the solid polymer, differing from it only in concentration and not fundamentally in structure.

The earlier data for polystyrene-xylene solutions<sup>3</sup> at 25° are also plotted in Fig. 7. In the concentration range studied, up to 52% polymer, the proportionality of  $\bar{G}$  to  $c^3$  also holds; the rigidities are smaller than those of the polyisobutylene solutions by about a factor of three. The polystyrene rigidities, however, do not extrapolate into the rigidity of the pure polymer (about  $5 \times 10^9$ ). This difference is undoubtedly associated with the fact that at 25° polyisobutylene is above, and polystyrene below, its brittle point. In the polystyrene-xylene system, the brittle transition must occur somewhere between 50 and 100% polymer at 25°.

**Origin of Rigidity.**—The rigidity observed in concentrated solutions of polyisobutylene and other polymers is no doubt due to storage of elastic energy in the deformation of long chain molecules. This could be accomplished by bending and stretching of bonds, or orientation entropy (rubber-like elasticity), or twist against the hindering potential opposing free rotation around bonds. For tension applied to the ends of an isolated contorted molecule, Kuhn<sup>17</sup> has shown that the contributions to deformation from bond bending and stretching are extremely small. In an analysis of the other two mechanisms, he finds that the molecular spring constant (force per unit extension) is inversely proportional to the number of bonds for orientation entropy, and inversely proportional to the square of this number for twist against the hindering potential.

To apply these considerations to a concentrated solution, we suppose the presence of a transitory network structure, whose net points are entanglements where two chains happen to be tightly kinked around each other. Then the molecular spring is not the entire molecule but the average strand between two points of entanglement. The number of entanglements should be proportional to the square of the volume concentration; if the strands are sufficiently short compared with the total molecular length so that free ends are negligible, the number of strands should also be proportional to the square of the concentration and their average length should be inversely proportional to the first power.

It follows<sup>15</sup> that the network rigidity should be proportional to the square of the volume concentration for rubber-like elasticity, but to the cube of the concentration for twisting against hindered rotation. The experimental concentration dependence thus corresponds to the latter mechanism.

On the basis of the network hypothesis, the temperature independence of  $G/c^3$  would mean that in the polyisobutylene solutions the entangle-

(17) W. Kuhn, *Helv. Chim. Acta*, **29**, 609, 830, 1095 (1946).

ments are purely statistical, and not influenced by any perceptible energy differences. The similarity of the values in different solvents would have the same significance. The small differences which are observed could be attributed to differences in the entropy of entanglement, entanglements being slightly more probable in chlorobenzene, for example. A lower intrinsic viscosity, reflecting a greater tendency for the polymer chain to coil back on itself, should be associated with a greater entanglement probability<sup>18</sup> and hence a higher rigidity, in agreement with Table IV.

The network hypothesis predicts that the rigidity should be independent of molecular weight, provided the latter is high enough so that free ends outside entanglements can be neglected. Data are not yet available to test this conclusion.

From mechanical measurements at much higher frequencies on undiluted polyisobutylenes of low molecular weight, Mason and Baker<sup>19</sup> have also postulated an elastic mechanism involving twisting of the polymer chains.

**Interpretation of Model Constants.**—If  $\bar{G}$  (Table VI) represents the hindered rotation elasticity mechanism,  $\eta_S$  could represent relaxation by rotation over the barriers or by slippage at entanglement points. Probably both mechanisms should occur, in different frequency ranges. According to Kuhn,<sup>17</sup> the former should be represented by a single relaxation time, directly propor-

(18) A lower intrinsic viscosity means that in very dilute solution a smaller volume is pervaded by the average polymer coil. In concentrated solution, also, the volume pervaded is probably smaller. In concentrated solution, however, the domain of each coil is thoroughly interlaced by other molecules. The number of entanglements per cc. should be practically independent of the size of coil domain; but it should be markedly influenced by local chain configuration, back kinking giving rise to "snagging," and hence higher entanglement probability.

(19) W. P. Mason, W. O. Baker, H. J. McSkimin and J. H. Heiss, *Phys. Rev.*, **73**, 1074 (1948).

tional to the number of bonds involved; for the network, then, the relaxation time should be inversely proportional to concentration, and  $\eta_S$  should be proportional to  $c^2$ . This appears to be the case for the chlorobenzene solutions. However, measurements should be extended to a broader frequency range before a detailed interpretation is attempted.

#### Summary

1. The propagation of transverse waves in solutions of polyisobutylene ( $\bar{M}_n = 1,200,000$ ) in *n*-heptane, xylene, iso-octane, and chlorobenzene has been studied as a function of frequency, temperature, and concentration.

2. The rigidity  $\bar{G}$  increases only slightly with frequency in the range from 100 to 1000 cycles/sec.

3. At constant weight concentration,  $\bar{G}$  decreases slightly with increasing temperature; at constant volume concentration ( $c$ ),  $\bar{G}$  is independent of temperature.

4. The rigidity is proportional to  $c^3$ ; in the different solvents, the ratio  $\bar{G}/c^3$  increases slightly in the order named above, which is also the order of decreasing intrinsic viscosities (at 20°).

5. The damping index,  $\lambda/x_0$ , decreases with increasing frequency or passes through a minimum.

6. The dispersion of rigidity and damping in chlorobenzene solutions can be fitted by a retarded Maxwell element with a ratio of parallel to series viscosity of 0.013.

7. The concentration dependence of  $\bar{G}$  can be interpreted in terms of a transient network structure with storage of elastic energy by twist against potentials opposing free rotation about bonds in the chains.

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RECEIVED AUGUST 30, 1948

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

## Variation of Monomer Pressure with Degree of Conversion in Emulsion Polymerization of Butadiene and of Butadiene-Styrene<sup>1</sup>

BY E. J. MEEHAN

### Introduction

During a polymerization reaction the pressure of the unpolymerized monomer decreases as the reaction proceeds to completion. The way in which the pressure changes with the degree of conversion of monomer to polymer depends upon the monomer and upon the nature of the polymerization system. Different relations between pressure and conversion are observed in a homogeneous system (solution or bulk polymerization) and

in a heterogeneous system (emulsion polymerization).

Pressure measurements can yield certain information about the nature of the polymerization system. Thus in a homogeneous system pressure measurements gave directly the value of the monomer activity in the thermal polymerization of pure styrene.<sup>1a</sup> In the emulsion polymerization of a monomer which is only slightly soluble in water, the unreacted monomer is present as a separate (oil) phase during the earlier part of the reaction; in the latter part of the reaction the unre-

(1) This Investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(1a) Walling, Briggs and Mayo, *This Journal*, **68**, 1145 (1946).