previous work.[20,21] Apparently the ions of metals which catalyze the hydrolysis of phosphate bonds are most effective at the *p*H at which precipitation of the insoluble hydroxide begins. It was previously suggested[21] that supersaturation of the hydroxide may be involved. On the other hand, the active catalyst may be ionic species such as $La(OH)_2^+$ or $Mg(OH)^+$. Catalysis of the hydrolysis of the secondary phosphate bonds of nucleic acid at *p*H 6 by magnesium ions is, however, not explained by these suggestions. The formation of a complex with magnesium ions very probably involves the phosphate groups of nucleic acid, and the small catalytic action at *p*H 6 may be due to changes in the phosphate ester bonds which may occur when the magnesium ion is complexed by the nucleate. It would be interesting to see if simple diester phosphates which do not complex magnesium ions also exhibit a catalyzed hydrolysis at *p*H 6 and 10. Catalysis would be expected at *p*H 10, but not at *p*H 6.

The potassium and magnesium nucleates have the same rates of hydrolysis in acidic and in alkaline solution. In 0.5 *N* base the activity of magnesium ion must be extremely low. On the other hand, acid can be used to displace magnesium from magnesium nucleate, as was discussed in the section on the preparation of potassium nucleate. In either case, acid and base are such effective catalysts that the effect of magnesium ion is negligible at high or low *p*H.

PRINCETON, NEW JERSEY

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[20] E. Bamann, *Angew. Chem.*, **52**, 185 (1939).

[21] J. E. Bacher and F. W. Allen, *J. Biol. Chem.*, **188**, 59 (1951).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Elastoviscous Properties of Polyisobutylene. VI. Relation between Stress Relaxation Modulus and Dynamic Modulus

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An idealized distribution function for the complete elastoviscous behavior of polyisobutylene is presented. From this function an exact expression for stress relaxation modulus as a function of time and temperature can be derived. It is shown to agree very closely with experimental values. An exact expression for the dynamic modulus is also calculated from the idealized distribution function and is available for experimental test.

Introduction

In Part V of this series,[1] the complete relaxation curve $E_{r,T}(t)$ for unfractionated polyisobutylene was presented. Empirical functions describing major portions of $E_{r,T}(t)$ were given, as were the corresponding distributions of relaxation times. The existence of a glassy, rubbery and transition region of elastoviscous behavior was demonstrated.

In this paper a complete idealized distribution of relaxation times giving an excellent fit with the relaxation of stress data $E_{r,T}(t)$ obtained thus far is given. The distribution of relaxation times consist of two discrete portions, the short time portion being molecular weight independent, and the long time portion being molecular weight dependent. From the idealized distribution of relaxation times analytical formulas for the relaxation modulus $E_{r,T}(t)$ and the dynamic modulus $E'_T(y)$ are derived.

The Idealized Distribution of Relaxation Times.—The distribution of relaxation times $D(\tau)$ for any (sufficiently high) molecular weight and for any temperature will be given the idealized representation

$$\frac{298}{T} D(\tau) = 0 \quad \tau < \tau_1 \tag{1}$$

$$\frac{298}{T} D(\tau) = M(\tau/\kappa)^{-1/2} \quad \tau_1 < \tau < \tau_2 \tag{2}$$

$$\frac{298}{T} D(\tau) = 0 \quad \tau_2 < \tau < \tau_3 \tag{3}$$

$$\frac{298}{T} D(\tau) = \frac{298}{T} E_0(\tau/\kappa)^{-1} \quad \tau_3 < \tau < \tau_m \tag{4}$$

$$\frac{298}{T} D(\tau) = 0 \quad \tau > \tau_m \tag{5}$$

In the equations $D(\tau)$ has the units dynes/cm.^{2} per hour and τ is expressed in hours. The parameters appearing in these equations have the values

$$\begin{gathered} M = 10^{3.95};\ E_0 = 7.2 \times 10^5;\ (\tau_1/\kappa) = 10^{-12.5} \\ (\tau_2/\kappa) = 10^{-5.4};\ (\tau_3/\kappa) = 1.39 \times 10^{-25}\ \bar{M}_v^{3.30} \\ (\tau_m/\kappa) = 1.53 \times 10^{-19}\ M_v^{3.30} \end{gathered} \tag{6}$$

where $\bar{M}_v$ is the viscosity average molecular weight and κ is a tabulated function of temperature which has the value unity at 25°.[1-3] For polyisobutylene sample N.B.S. the following values were used

$$\tau_3 = 10^{-4.34};\ \tau_m = 10^{1.70} \tag{6a}$$

A plot of the idealized distribution of relaxation times for polyisobutylene (sample N.B.S.[4]) is shown (solid line) in Fig. 1. The plot is in the form $D'(\log \tau)$ *versus* $\log \tau$. The relation between $D'(\log \tau)$ and $D(\tau)$ is: $D'(\log \tau) = 2.303\ \tau\ D(\tau)$. As can be seen in the figure $D'(\log \tau)$ consists of a wedge and a box. Change of temperature merely adds a constant to the logarithmic relaxation time scale plotted along the abscissa. Changing the molecular weight at a fixed temperature leaves the position of the wedge unaltered, but causes a horizontal translation of the box along the abscissa, so that for larger molecular weights the wedge and the box are separated more widely.

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[1] A. V. Tobolsky and J. R. McLoughlin, *J. Polymer Sci.*, **5**, 43 (1952).

[2] R. D. Andrews, N. Hofman Bang and A. V. Tobolsky, *ibid.*, 3 669 (1948).

[3] R. D. Andrews and A. V. Tobolsky, *ibid.*, **6**, 221 (1951).

[4] The abbreviation N.B.S. stands for National Bureau of Standards.

The relaxation modulus $E_{r,T}(t)$ which is obtained from the distribution of relaxation times (1)–(5) is

$$\frac{298}{T}E_{r,T}(t) = M(t/\kappa)^{-1/2}[\Gamma_{t/\tau_1}(1/2) - \Gamma_{t/\tau_2}(1/2)] + \frac{298}{T}E_0\,[E_i\,(-t/\tau_3) - E_i(-\,t/\tau_m)] \quad (7)$$

where $\Gamma_x(1/2)$ is the incomplete γ-function[5] of the argument $^1/_2$ and $E_i(-x)$ is the exponential integral function.[6]

Values of $E_{r,298}(t)$ obtained from equation (7) are given in Table I. These values are calculated for the parameters given in 6a. Experimental values[1,3,7] for $E_{r,298}(t)$ for unfractionated polyisobutylene (sample N.B.S.) are also shown in Table I. The experimental values were obtained from the composite relaxation curve at 298°K. constructed from the individual relaxation curves obtained at numerous temperatures.

TABLE I

log (t) or log (y), t and y expressed in hours	log $E_{r,298}(t)$, experimental	log $E_{r,298}(t)$, computed by Eq. 7	log $E'(y)$, computed by Eq. 10
−14.0		10.50	10.50
−13.5		10.50	10.50
−13.0		10.46	10.49
−12.5		10.38	10.44
−12.0		10.20	10.27
−11.5		9.94	10.08
−11.0		9.70	9.81
−10.5		9.45	9.55
−10.0	9.22	9.20	9.30
− 9.5	8.97	8.94	9.05
− 9.0	8.71	8.70	8.80
− 8.5	8.45	8.44	8.55
− 8.0	8.20	8.20	8.31
− 7.5	7.96	7.94	8.07
− 7.0	7.70	7.70	7.81
− 6.5	7.45	7.48	7.56
− 6.0	7.25	7.24	7.32
− 5.5	7.11	7.08	7.12
− 5.0	7.02	7.00	7.02
− 4.5	6.93	6.98	6.99
− 4.0	6.91	6.96	6.97
− 3.5	6.87	6.92	6.94
− 3.0	6.84	6.87	6.89
− 2.5	6.80	6.82	6.84
− 2.0	6.76	6.74	6.79
− 1.5	6.70	6.69	6.73
− 1.0	6.62	6.61	6.65
− 0.5	6.53	6.51	6.56
0.0	6.40	6.38	6.45
0.5	6.22	6.21	6.30
1.0	5.96	5.94	6.07
1.5	5.62	5.49	5.66

For computed values of $E_{r,298}(t)$ larger than $10^{7.2}$ dynes/cm.^{2} the relaxation function (equation (7)) is almost wholly determined by the first term on the right-hand side of equation (7); namely, from the portion of $D(\tau)$ embodied in equation (2), which is molecular weight independent. For computed values of $E_{r,298}(t)$ smaller than $10^{7.0}$ dynes/cm.^{2} the function is almost wholly determined by the second term on the right-hand side of equation (7); namely from the portion of $D(\tau)$ embodied in equation (4); which is strongly dependent on molecular weight.

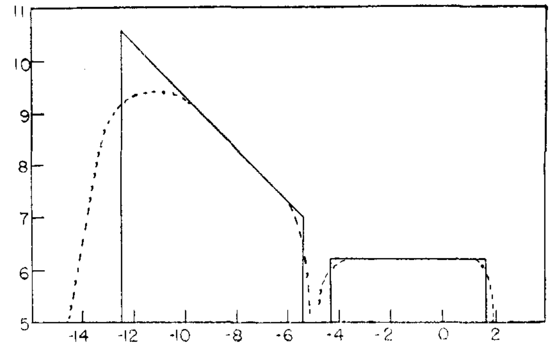

Fig. 1.—log D'(log τ) *versus* log τ $D'(\tau)$ expressed in dynes/cm.^{2}; τ expressed in hours. Solid lines represent idealized distribution. Dotted lines represent "true" distribution (schematic).

As can be seen from Table I, the agreement between experimental values of $E_{r,298}(t)$ and the values computed from equations (6) and (7) are quite good. Experimental values for time values smaller than 10^{-10} hour (*i.e.*, values of relaxation modulus larger than $10^{9.22}$ dynes/cm.^{2}) are not yet available.

The Exact Distribution of Relaxation Times.—The theoretical equation for $E_{r,298}(t)$, according to equation (7) and based on the idealized distribution function (1)–(6) is shown plotted as a solid line in Fig. 2. The experimental points, which are known for values of $E_{r,298}(t)$ smaller than $10^{9.22}$ dynes/cm.^{2} are shown in this figure as open circles. For values of $E_{r,298}$ (t) larger than $10^{9.22}$ dynes/cm.^{2} experimental values are not yet available. However, it is to be expected (from comparison with similar data in a different temperature range obtained on polymethyl methacrylate[1]) that the experimental values of $E_{r,298}(t)$ in this range will not approach the maximum low temperature value quite so sharply as the solid curve based on equation (7) shown in Fig. 2. For pur-

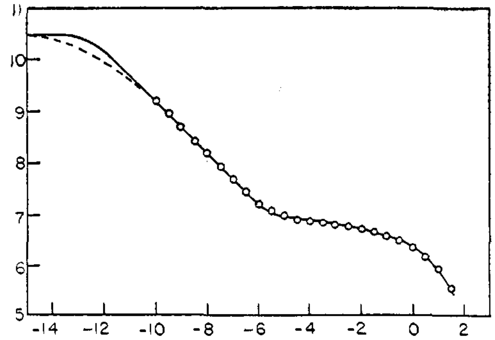

Fig. 2.—log $E_{r,298}(t)$ *versus* log(t). $E_{r,298}(t)$ expressed in dynes/cm.^{2}; t expressed in hours. Solid line represents calculated value of log $E_{r,298}(t)$ according to equation (7). Open circles represent experimental points. Dotted line represents a guess as to the experimental values of $E_{r,298}(t)$ in the range where measurements are still lacking.

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[5] Karl Pearson, "Tables of the Incomplete Γ Function," His Majesty's Stationery Office, 1922.

[6] Tables of Sine, Cosine and Exponential Integrals (2 vols.). W.P.A. Tables, New York, N. Y., 1940.

[7] G. M. Brown and A. V. Tobolsky, *J. Polymer Sci.*, **6**, 165 (1951).

poses of graphic demonstration a dotted line is shown in Fig. 2 to portray what might be expected to be the "experimental" curve in this range.

The "true" distribution of relaxation times corresponding to the "experimental" dotted curve is also pictorially presented as a dotted curve in Fig. 1. This must of course also be regarded as a schematic diagram. It points out the fact that the true distribution function $D'(\log \tau)$ will probably show rounding off at τ_1, τ_2, τ_3 and τ_m as compared with the idealized distribution function (1)–(6).

There is a very distinct advantage, however, in using the idealized distribution function. This function has enabled us to calculate the relaxation modulus $E_{r,298}(t)$ in terms of tabulated functions. It will be shown in the succeeding section that it also enables us to calculate dynamic modulus (and if we desire, dynamic viscosity) in terms of closed analytic expressions which can be readily computed and checked with experimental results.

The Calculation of Dynamic Modulus.—The formulas for dynamic modulus and dynamic viscosity as functions of angular frequency of vibration and of the distribution of relaxation times were first given by Tobolsky and Eyring.[8]

$$E_{\text{dyn}} = \int \frac{w^2\tau^2}{1 + w^2\tau^2} D(\tau)\, d\tau \quad w = \text{angular frequency} \tag{8}$$

$$w\eta_{\text{dyn}} = \int \frac{w\tau}{1 + w^2\tau^2} D(\tau)\, d\tau \tag{9}$$

The same formulas were later also given by Alfrey and Doty,[9] Kuhn, *et al.*,[10] and by Ferry.[11] These workers used the notation of a complex modulus $E = E' + iE''$, where E' is identical with the dynamic modulus E_{dyn} and E'' is identical with $w\eta_{\text{dyn}}$. We shall use the notation $E'_{298}(y)$ to represent the dynamic modulus in tension at 298°K. in terms of the variable $y = 1/w$. The quantity y has the dimensions of time.

If the distribution function (equations (1)–(5)) is substituted in equation (8) one obtains

$$E'_{298}(y) = \left[\frac{M}{2(2y)^{1/2}} \ln \frac{\tau^{-1}y + \tau^{-1/2}(2y)^{1/2} + 1}{\tau^{-1}y - \tau^{-1/2}(2y)^{1/2} + 1}\right]_{\tau_2}^{\tau_1} + \left[\frac{M}{(2y)^{1/2}} \tan^{-1} \frac{\tau^{-1/2}(2y)^{1/2}}{1 - \tau^{-1}y}\right]_{\tau_2}^{\tau_1} + \frac{E_0}{2} \ln \frac{y^2 + \tau_m^2}{y^2 + \tau_3^2} \tag{10}$$

where

$$y = 1/w \tag{11}$$

A similar closed expression can be written for $E''_{298}(y)$.

Values of log $E'_{298}(y)$ as computed from equation (10) for various values of y are given in Table I. In this table y is expressed in hours. The dynamic shear modulus, which is the quantity obtained experimentally, is one third times $E'(y)$. Experimental data are now being accumulated by various workers which will put the predicted values of $E'(y)$ to a severe experimental test.

Materials.—The polyisobutylene (sample N.B.S.) to which reference has been made throughout this paper, is a sample which was distributed by the National Bureau of Standards to various research laboratories. The molecular weight $\bar{M}_v$ of this unfractionated sample is reported as 1.35 × 10^6. This value of $\bar{M}_v$ would give rise to τ_3 and τ_m values of $10^{-4.65}$ and $10^{1.39}$ hours at 25°, according to equation (6).

I have used values of τ_3 and τ_m equal to $10^{-4.34}$ and $10^{1.70}$ hours, respectively, because they give a somewhat better fit with experiment. The experimental values of $E_{r,298}(t)$ for magnitudes below 10^7 dynes/cm.^{2} were taken from a report by Andrews[12] and Tobolsky to the N.B.S. The values of $E_{r,298}(t)$ for magnitudes larger than 10^7 dynes/cm.^{2} were taken from references (6) and (1).

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PRINCETON, NEW JERSEY

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[8] A. V. Tobolsky and H. Eyring, *J. Chem. Phys.*, **11**, 125 (1943).

[9] T. Alfrey and P. Doty, *J. Applied Phys.*, **16**, 700 (1945).

[10] W. Kuhn, O. Kunzle and A. Preissmann, *Helv. Chim. Acta*, **30**, 307, 464, 839 (1947).

[11] J. D. Ferry, THIS JOURNAL, **72**, 3746 (1950).

[12] Soon to be published.