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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

The Effect of Rate of Shear on the Viscosity of Dilute Solutions of Polyisobutylene[1]

BY T. G FOX,[2] JR., J. C. FOX AND P. J. FLORY

Specific viscosities of dilute solutions of polyisobutylene fractions decrease approximately linearly with the rate of shear over the range from several hundred to several thousand sec.$^{-1}$. The "shear coefficient" ϕ, conveniently defined as $100 \times d(\ln \eta_{sp})/d\gamma$, is independent of concentration at low concentrations. For molecular weights not exceeding several million, ϕ is approximately proportional to the square of the intrinsic viscosity (as indicated by measurements on the same polymer fraction in different solvents), and inversely proportional to the molecular weight (as indicated by comparison of ϕ's in different solvents for polymers of molecular weights so chosen as to give the same intrinsic viscosities in the respective solvents). This empirical relationship is useful for the extrapolation of intrinsic viscosities of polyisobutylene solutions to zero rate of shear. The logarithm of η_{sp} decreases non-linearly with γ for dilute solutions of polyisobutylene of very high molecular weight (*ca.* 15×10^6).

The non-Newtonian behavior of polymer solutions generally has been ignored in the evaluation of the intrinsic viscosity, apparently on the assumption that the effect of rate of shear is eliminated in the extrapolation to zero concentration. An effect of rate of shear which is by no means negligible, however, has been reported by various investigators.[3,4,5,6] The change in the viscosity η with rate of shear γ does indeed vanish as the polymer concentration is decreased to zero. However, the manner in which the coefficient of the specific viscosity, $d(\ln \eta_{sp})/d\gamma$, (or $d \ln[\eta]/d\gamma$), depends on the concentration and molecular weight is not clearly established by previous investigations. Our preliminary measurements showed that the magnitude of this coefficient when the molecular weight is large is such as to require correction of viscosities measured in a conventional viscometer if accurate viscosities are required. This is especially important in cases where the rate of shear varies considerably, *e. g.*, as in the investigation of the effect of the temperature on the intrinsic viscosity measured at fixed shearing stress.

The present investigation was undertaken in order to establish empirical relationships by means of which to correct intrinsic viscosities to zero rate of shear. Viscosities of polyisobutylenes of widely differing molecular weights were measured in various solvents at different temperatures using a specially constructed Ostwald viscometer permitting measurements at rates of shear from several hundred to several thousand reciprocal seconds.

Experimental

Design and Use of the Viscometer.—The shearing stress S at the wall of the capillary of the viscometer is given by

$$S = rghd/2l \qquad (1)$$

where r and l are, respectively, the radius and the length of the capillary, h is the distance between the upper and lower levels of the liquid in the viscometer, g is the acceleration of gravity and d is the liquid density. The expression for the viscosity η is

$$\eta/d = \alpha(t - \beta/\alpha t) \qquad (2)$$

where t is the efflux time and α and β are constants of the instrument given by

$$\alpha = \pi g h r^4/8Vl \qquad (2a)$$
$$\beta = mV/8\pi l \qquad (2b)$$

Here V is the volume of fluid delivered in time t and m is an "end constant" dependent on the shapes of the ends of the capillary.[6]

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[1] This investigation was carried out at Cornell University in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

[2] Rohm and Haas Company, Inc., Philadelphia, Pa.

[3] H. Staudinger and H. Machemer, *Ber.*, **62**, 2921 (1929); H. Staudinger, "Die hochmolekulären organischer Verbindungen," Springer, Berlin, 1932, p. 188.

[4] E. O. Kraemer and F. J. Van Natta, *J. Phys. Chem.*, **36**, 3175 (1932).

[5] W. O. Baker, C. S. Fuller and J. H. Heiss, Jr., THIS JOURNAL, **63**, 3316 (1941).

[6] D. J. Mead and R. M. Fuoss, *ibid.*, **64**, 277 (1942). See also the recent paper by H. T. Hall and R. M. Fuoss, *ibid.*, **73**, 265 (1951).

For the experiments reported here a viscometer was required wherein the rate of shear may be accurately varied over a wide range. Simplicity of design and manipulation and a low kinetic energy correction were also desired. The correction factor for kinetic energy is given by $(1 - \beta/\alpha t^2)$, which is approximately equal to $[1 - \beta\alpha/(\eta/d)^2]$. Since the product $\beta\alpha$ is proportional to hr^4/l^2, it is best to vary the shearing stress by varying h, keeping l large and r as small as possible.

All of these objectives, and the advantages inherent in the use of a single instrument, were achieved through the use of an Ostwald type viscometer constructed as shown in Fig. 1. It consists of a 20-cm. length of capillary of radius 0.030 cm., with two efflux bulbs about 20 cm. apart, and a large reservoir of appropriate dimensions. The viscometer was mounted vertically in a constant temperature bath controlled to ±0.01°. Various values of h between 3.5 and 45 cm. were obtained through the use of one or the other of the efflux bulbs and by pipetting various quantities of liquid into the viscometer (Table I) in order to adjust the level in the reservoir appropriately. Efflux times were observed with an accurate stopwatch reading to 0.01 sec.

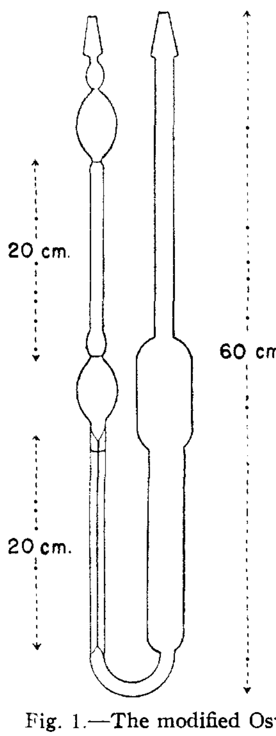

Fig. 1.—The modified Ostwald viscometer for measuring viscosities at different shearing stresses. The diameter of the capillary is 0.060 cm.; the volumes of the upper and lower efflux bulbs are approximately 10 and 5 ml., respectively.

Calibration of the Viscometer.—The kinetic energy correction term β/α was determined at each filling by measuring the efflux times for water at 20, 37.8 and 54.4°.[7] The results are given in Table I. The correction on the efflux time for water at 20° due to the kinetic energy loss varies from 1.43 to 0.10% from the highest to the lowest stress values employed. The corresponding correction in a Ubbelohde No. 1 viscometer is approximately 2%.

Materials.—Two polyisobutylenes were fractionated by the addition of acetone to their benzene solutions at 30°.[8] Three of the fractions so obtained were chosen for this study. Their molecular weights as calculated from intrinsic viscosities in diisobutylene at 20° (measured in a Ubbelohde No. 1 viscometer) using the following equation[8]

$$[\eta] = 3.6 \times 10^{-4} \bar{M}_v^{0.64} \qquad (3)$$

were 15,000,000 (approx.), 1,460,000 and 460,000.

Table I

Calibration of Kinetic Energy Correction Term for the Special Viscometer

Vol. of fluid in viscometer in ml.[a]	Efflux bulb used	Av. value of h in cm.	Efflux time for water at 20°, sec.	β/α	Corrn. in t for water at 20° = $100\beta\alpha$, %
17.6	Lower	21	143.27	280	1.43
35.2	Upper	45	178.29	350	1.14
52.8	Lower	12	167.51	165	0.61
70.4	Upper	36	297.63	295	.34
70.4	Lower	7.0	457.02	454	.22
88.0	Lower	3.5	966.50	964	.10

[a] The pipet delivered 17.6 ml. at 20°. It was kept at room temperature, quickly filled to the mark with the liquid at the temperature of the bath, and the contents were delivered immediately to the viscometer allowing 30 sec. for drainage.

Results and Discussion

Using the polyisobutylene fraction of M = 1,460,000, the specific viscosity was determined at 40° as a function of rate of shear in several solvents at concentrations so chosen that the relative viscosity η_r generally ranged from 1.2 to 1.9. In Figs. 2 and 3 typical results are plotted as log η_{sp} *vs.* the maximum rate of shear. The latter was calculated from the maximum stress S using the equation

$$\gamma = S/\eta = rhgd/2l\eta_r\eta_0 \qquad (4)$$

where η_0 is the viscosity of the solvent. The data are represented by straight lines corresponding to the relationship

$$\ln \eta_{sp} = [\ln \eta_{sp}]_0 - (\phi/100)\gamma \qquad (5)$$

where $[\ln \eta_{sp}]_0$ is the value of $\ln \eta_{sp}$ at zero rate of shear and

$$\phi = 100\, d(\ln \eta_{sp})/d\gamma \qquad (5a)$$

represents the percentage decrease in the observed specific viscosity per unit increase in the shear rate. The values of ϕ in a given solvent are independent of concentration as illustrated in Fig. 2 where the data for different concentrations of this polyisobutylene fraction in cyclohexane are represented by a set of parallel straight lines. Both $[\eta]$ and ϕ are lower the poorer the solvent (Table II and Fig. 3); a plot of ϕ *vs.* $[\eta]^2$ (Fig. 4) shows that for a given molecular weight ϕ increases approximately as the square of the intrinsic viscosity.

Table II

Intrinsic Viscosity—Rate of Shear Data for Solutions of Polyisobutylene

M	T, °C.	Solvent	$[\eta]$	$\phi_{obsd.}$, %/sec.$^{-1}$ × 10^3	$\phi_{calcd.}$, %/sec.$^{-1}$ × 10^1
15,000,000	40	C_6H_{12}	(25)		4.6
15,000,000	40	Toluene	(15)		1.6
1,460,000	40	C_6H_{12}	5.20	2.2 ± 0.2	2.0
1,460,000	40	CCl_4	(4.6)	1.9 ± 0.2	1.6
1,460,000	40	Diisobutylene	3.3	0.8 ± 0.1	0.82
1,460,000	40	*n*-Heptane	3.1	.5 ± 0.25	.72
1,460,000	40	Toluene	3.05	.7 ± 0.1	.71
1,460,000	40	C_6H_6	2.1	.3 ± 0.2	.32
1,460,000	10	C_6H_{12}	5.20	2.4 ± 0.5	2.0
460,000	40	C_6H_{12}	(2.3)	0.8 ± 0.4	1.2
		Diisobutylene	(1.5)	0.5 ± 0.1	0.54

Both ϕ and $[\eta]$ for the fraction of molecular weight 1,460,000 in cyclohexane remain unchanged

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[7] A. S. T. M. Designation D445-39T.

[8] P. J. Flory, This Journal, **65**, 372 (1943).

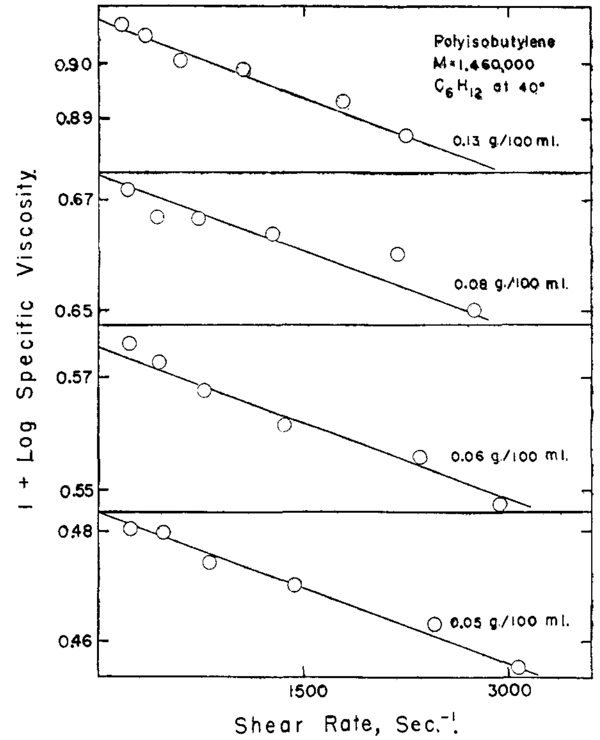

Fig. 2.—log η_{sp} *vs.* rate of shear for various concentrations of the polyisobutylene fraction of M = 1,460,000 in cyclohexane at 40°.

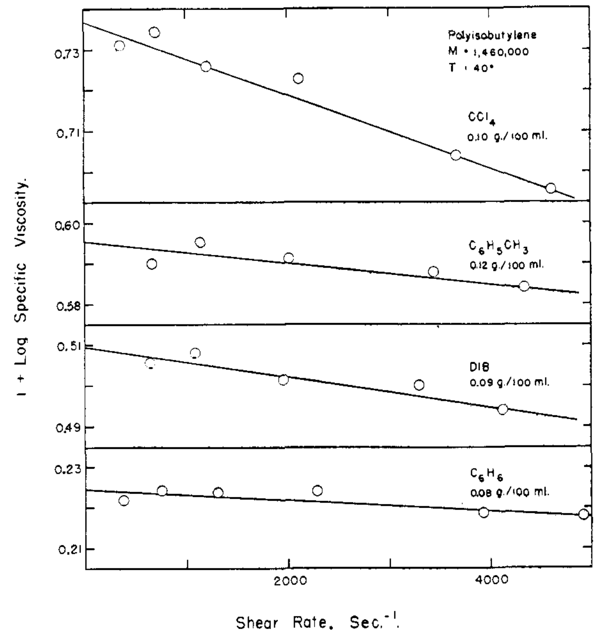

Fig. 3.—log η_{sp} *vs.* rate of shear for the polyisobutylene of M = 1,460,000 in various solvents at 40°.

when the temperature is reduced from 40° to 10°. Presumably the percentage decrease in ϕ with decreasing temperature would be greater in poorer solvents where the intrinsic viscosity–temperature coefficient is higher, but the precision of the determination of the low ϕ values in poor solvents is insufficient for the detection of such changes.

For solutions of the polyisobutylene of lowest molecular weight (M = 460,000) the relationship between ln η_{sp} and γ was also linear and independent of concentration though dependent on solvent (Table II). Solutions of the polymer of highest molecular weight ($M = 15 \times 10^6$), however, exhibited a decidedly non-linear dependence of ln η_{sp} on γ over the range investigated (Fig. 5). Thus, the present equations must not be employed for molecular weights exceeding several million. For polymers of molecular weight below this limit, the approximate empirical expression

$$\phi = 1.1 \times 10^2[\eta]^2/M \qquad (6)$$

adequately reproduces values of the shear coefficient ϕ within the experimental error, according to the comparisons shown in Table II between observed and calculated values.

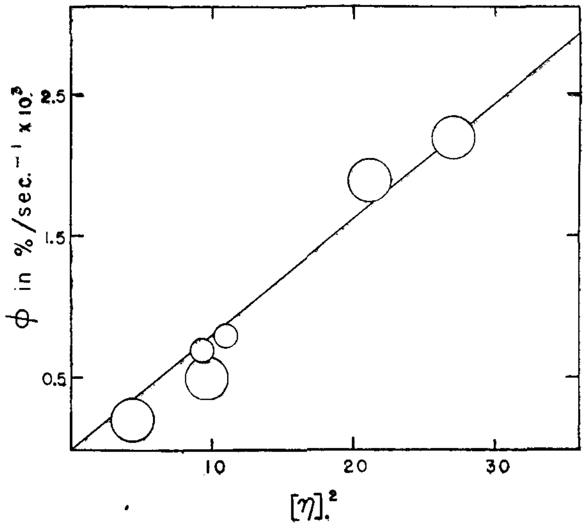

Fig. 4.—ϕ *vs.* $[\eta]^2$ at 40° for the polyisobutylene fraction of M = 1,460,000 in various solvents.

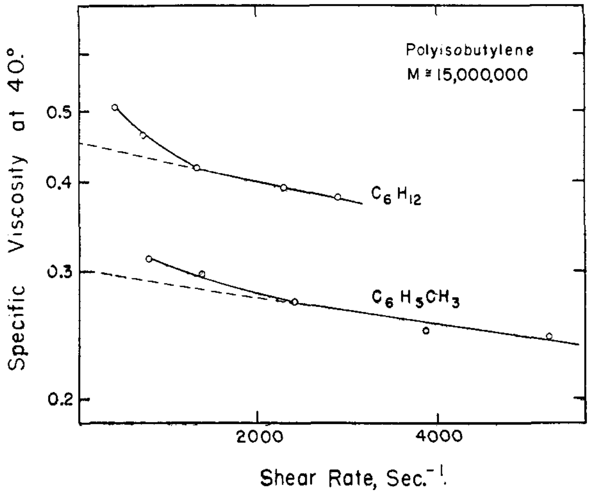

Fig. 5.—Semi-logarithmic plot of η_{sp} *vs.* shear rate at 40° for the polyisobutylene fraction of $M \cong$ 15,000,000 in cyclohexane and in toluene.

It is unlikely that equations (5) and (6) can be applied to more concentrated solutions of polyisobutylene, or at much higher rates of shear than were employed here. Furthermore, a preliminary investigation[9] on dilute solutions of GR-S fractions indicates an increase in ϕ with increasing concentration. It may be significant that the ϕ values for the GR-S solutions were two to three times higher than those for the present polyisobutylene solutions.

It is important to note that the ratio of η_{sp}/c at zero rate of shear to its value as ordinarily measured in a viscometer operating at a standard shearing *stress* increases as the concentration is decreased. This circumstance arises because γ decreases with increasing concentration owing to the increase in viscosity. Ordinary extrapolation to infinite dilution applied to measurements made with a single viscometer fails, therefore, to reduce the magnitude of the error arising from non-Newtonian flow. This is especially important for high molecular weight polymers in good solvents. Failure to correct for this non-Newtonian effect will, for example, distort the observed viscosity–temperature and viscosity–concentration relationships. In order to obtain an accurate value of the intrinsic viscosity, it is necessary to carry out a suitable extrapolation to zero rate of shear. Employing equations (5) and (6), it is now possible to make such extrapolations for solutions of polyisobutylene for which $M < 2 \times 10^6$ and $\eta_r < 2$.

Certain qualitative observations concerning the dependence of ϕ on $[\eta]$ and M expressed in equation (6) can be made. According to this equation, the departure from Newtonian behavior for solutions of a given polyisobutylene fraction is greater in a good than in a poor solvent, ϕ increasing approximately as $[\eta]^2$. In the better solvent, the volume of the domain of a single polymer molecule is larger. The number of intrachain entanglements is thus diminished and hence the polymer is more deformable. Since the forces acting on the coiled polymer molecule increase as the volume of the domain increases, and since these forces presumably become more effective in distorting and orienting the polymer molecule in the flow field as the deformability increases, both of these factors may contribute toward the observed increase in ϕ. On the other hand, if polyisobutylenes of different M are dissolved in different solvents so chosen that the intrinsic viscosities are equal, the value of ϕ will be lower for the polymer of highest molecular weight. This may be explained by a higher concentration of intrachain entanglements in the more densely populated domain of the high molecular weight polymer, which therefore is rendered less deformable.

The above linear relationship between ln η_{sp} and γ does not agree with the predictions of the theory of Kuhn and Kuhn[10] according to which η_{sp} should decrease initially with γ^2.

[9] Unpublished results obtained in these laboratories.

[10] W. Kuhn and H. Kuhn, *J. Colloid Sci.*, **3**, 11 (1948).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Treatment of Intrinsic Viscosities[1]

BY P. J. FLORY AND T. G FOX, JR.

An improved derivation is given for the relationship between the configurational dimensions of a polymer molecule in solution and the thermodynamic interaction between polymer segments and solvent molecules. The connection between intrinsic viscosity and molecular configuration is discussed in the light of recent theories, and general procedures for treating intrinsic viscosity data are given. The root-mean-square end-to-end distance for the polymer molecule when the net thermodynamic interaction between segments and solvent is zero may be computed from suitable viscosity measurements. The influence of hindrance to free rotation on the polymer configuration, unperturbed by thermodynamic interactions with the solvent medium, is obtained directly from this dimension. The influence of thermodynamic interactions on chain dimensions is considered separately. Parameters expressing the heat and entropy of dilution of polymer segments with solvent may be deduced from intrinsic viscosity measurements at different temperatures.

Introduction

In the treatment of the properties of very dilute polymer solutions it is convenient to represent the molecule as a statistical distribution of chain elements, or segments, about the center of gravity. The average distribution of segments for a chain polymer molecule is approximately Gaussian[2]; its breadth depends on the molecular chain length and on the thermodynamic interaction between polymer segments and solvent. The intrinsic viscosity may be regarded as a measure of the ratio of the effective hydrodynamic volume V_e of the polymer in a given solvent to its molecular weight M; *i. e.*, $[\eta] \propto R_e^3/M$. The recent theories of Debye and Bueche,[3] Kirkwood and Riseman,[4] and of Brinkman[5] show that for sufficiently large chain lengths the effective hydrodynamic radius R_e must vary directly with a linear parameter of the Gaussian distribution characterizing the polymer in solution. Convenient linear parameters for this purpose are the root-mean-square distance $\sqrt{\overline{r^2}}$ between the ends of the polymer chain, or the root-mean-square distance $\sqrt{\overline{s^2}}$ of the segments from the center of gravity (*i. e.*, the radius of gyration of the dissolved molecule). The above conclusion had been anticipated previously by various authors[6] but the recent

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[1] This investigation was carried out at Cornell University in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

[2] P. Debye and I. M. Krieger (unpublished) have shown that the average distribution of each segment about the center of gravity is exactly Gaussian for a random chain unperturbed by intramolecular interactions.

[3] P. Debye and A. M. Bueche, *J. Chem. Phys.*, **16**, 573 (1948).

[4] J. G. Kirkwood and J. Riseman, *ibid.*, **16**, 565 (1948).

[5] H. C. Brinkman, *Applied Sci. Res.*, **A1**, 27 (1947).

[6] W. Kuhn, *Kolloid Z.*, **68**, 2 (1934); W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **26**, 1394 (1943); P. J. Flory, *J. Chem. Phys.*, **13**, 453 (1945).