[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, AMERICAN VISCOSE CORPORATION]

Factors Affecting the Non-Newtonian Viscosity of Rigid Particles[1]

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The viscosities of two poly-γ-benzyl-L-glutamate samples and a mixture of them were measured as a function of shearing stress τ (up to 10^6 dynes cm.$^{-2}$) in *m*-cresol in which the polypeptides exist as rod-like α-helices. Marked reduction in the intrinsic viscosity $[\eta]$ (to less than 5% of its value at $\tau = 0$ for the high molecular weight sample) can be achieved at the highest attainable τ. The data support previous findings[2] thus further confirming the validity of the viscosity theories for rigid particles. The shear dependence of $[\eta]$ of a rigid system gives a composite curve independent of solvent viscosity and temperature T when $[\eta]$ is plotted against τ/T. The critical shearing stress τ_c (above which the viscosity drops sharply) depends upon the size and shape of the polymers. The longer the particles, the smaller is the τ_c. The effect of polydispersity results in a broadening of the non-Newtonian region and gives higher apparent length L_{app} at lower rate of shear D. The mean length at zero shear, however, is smaller than L_{app} under finite shear. The controversy on the so-called power law of viscosity is partly attributed to the effect of polydispersity which can cause the viscosity to obey a pseudo-odd function of τ or D.

Introduction

The shear dependence of the viscosity of polymer solutions has been troublesome in the determination of size and shape of the macromolecules. The interpretation of their intrinsic viscosity has often been complicated by the uncertainty involved in the arbitrary extrapolation of the viscosity to zero rate of shear. In a previous publication,[2] however, it was shown that advantage can be taken of the marked difference in non-Newtonian behavior between rigid particles and random coils for the characterization of configurations or configurational changes. For rigid particles the intrinsic viscosity at high shearing stress can be reduced to less than $^1/_{10}$ of its original value, which is in striking contrast to the mild drop in viscosity for the corresponding polymers in randomly coiled form. Furthermore, the shear dependence of intrinsic viscosity of an α-helical poly-γ-benzyl-L-glutamate (PBLG) solution completely confirmed the viscosity theories for rigid particles[3-5] thus developing a new method for determining the rotary diffusion constant Θ and thereby the shape of the particles. Recently two additional PBLG samples became available to us. It seemed appropriate further to test the validity of the theories and also to determine the effect of various factors on the shear dependence of viscosity. This paper will therefore describe the effect of molecular weight, degree of polydispersity, solvent viscosity and temperature on the non-Newtonian viscosity of rigid particles.

Experimental Details

A. Materials.—Two poly-γ-benzyl-L-glutamate samples (Code Nos. PBLG 421 and 397) were obtained through the courtesy of Dr. E. R. Blout and Professor P. Doty. Their molecular properties were: M_w = 130,000 and 336,000[6]; M_n = 117,000 and 253,000[7]; L_w (rods) = 890 and 2300 Å. (assuming the length per monomer residue as 1.5 Å.), respectively.

The reagent-grade solvent, *m*-cresol (Fisher Scientific Company), was redistilled before use.

B. Viscosity Measurements.—A stainless steel capillary viscometer was used for the viscosity measurements. It was built by the Franklin Institute, Philadelphia, and its basic design has been described elsewhere.[8] The dimensions of several capillary tubes are listed in Table I. The applied pressure (dry nitrogen gas) can be varied from 2 cm. water to a maximum limit of about one hundred atmospheres. The viscosity η defined as the ratio of the shearing stress τ to the rate of shear D was calculated from the equations

TABLE I

DIMENSIONS OF CAPILLARY TUBES

Capillary no.	Length *L*, cm.	Radius *R*, cm.	*L*/*R*
1	30.485	0.2527	121
2	30.485	.1217	251
4	30.485	.06109	500
8	1.521	.01493	102
9	7.625	.01496	510
11	0.150	.00530	28

$$\tau = \Delta P(R/2L) \tag{1}$$

and

$$D = 4Q/\pi R^3 \tag{2}$$

where ΔP is the applied pressure, Q the volume flow rate and R the radius and L the length of the capillary, τ being maximum at the capillary wall. The experimental D in eq. 2 was further corrected for the inhomogeneous flow in a capillary by the relation[9]

$$D_{cor} = D_{exptl}\,(n + 3)/4 \tag{3}$$

where n is the slope of the log D–log τ plot at any τ (or D). The well-known Kroepelin equations[10] for the mean rate of shear $\bar{D}$

$$\bar{D} = 8Q/3\pi R^3 \tag{4}$$

and the mean shearing stress τ

$$\bar{\tau} = \Delta P(R/3L) \tag{5}$$

were not used here, since they are valid only for Newtonian flow. It should, however, be pointed out that eq. 3 is also not exact since it is derived from the power law

$$D = k\tau^n \tag{6}$$

at any chosen τ (or D) (k being a constant) and by assuming a constant n across the capillary. Actually n is unity at the center of the capillary where the flow is Newtonian and greater than one toward the wall of the capillary where the flow is non-Newtonian. In a previous publication,[2] how-

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[1] Presented at the 135th American Chemical Society Meeting, Boston, April, 1959.

[2] J. T. Yang, THIS JOURNAL, **80**, 1783 (1958).

[3] N. Saito, *J. Phys. Soc. Japan*, **6**, 297 (1951).

[4] J. G. Kirkwood, *Rec. trav. chim.*, **68**, 649 (1949); J. G. Kirkwood and P. L. Auer, *J. Chem. Phys.*, **19**, 281 (1951); J. G. Kirkwood and R. J. Plock, *ibid.*, **24**, 665 (1956).

[5] H. A. Scheraga, *ibid.*, **23**, 1526 (1955).

[6] P. Doty, A. M. Holtzer, J. H. Bradbury and E. R. Blout, THIS JOURNAL, **76**, 4493 (1954); P. Doty, J. H. Bradbury and A. M. Holtzer, *ibid.*, **78**, 947 (1956).

[7] P. Doty and J. T. Yang, manuscript in preparation.

[8] W. Philippoff, *Kolloid-Z.*, **75**, 2 (1936); F. H. Gaskins and W. Philippoff, paper presented at the Christmas Symposium on Non-Newtonian Fluids in Science and Engineering, Division of Industrial and Engineering Chemistry, American Chemical Society, Pittsburgh, Pennsylvania, 1958.

[9] W. Philippoff, "Viskosität der Kolloide," Steinkopff, Dresden, 1942, p. 42.

[10] H. Kroepelin, *Kolloid Z.*, **47**, 291 (1929).

ever, eq. 1, 2 and 3 rather than eq. 4, 5 and 3 gave very good agreement between theory and experimental results and appeared quite adequate for the purpose of our calculations.

The intrinsic viscosity $[\eta]$ at constant shearing stress was calculated according to Martin's equation.[11] Although thirty or more experimental points were measured for each flow curve, the precision of the data was greatly improved by drawing a smooth curve through the points and using smoothed values to calculate $[\eta]$. At very high stress the intrinsic viscosity values were unavoidably less accurate due to the small difference in viscosity between the solution and solvent. On the other hand, the kinetic energy correction for the *m*-cresol solution was negligible throughout the entire flow curve with the capillary tubes employed, even at the highest τ studied. Neither was turbulent flow present, since the Reynold's number for all the solutions studied was well below the critical range of 2000–4000.

Results

Three series of flow curves were measured in *m*-cresol at 25.0° over a wide range of shearing stresses (from 10 to 10^5 dynes cm.$^{-2}$). The series were on polymers: (1) PBLG 421, (2) PBLG 397 and (3) a mixture of 3 parts No. 421 and 1 part No. 397 (by weight). Four or five concentrations were employed for each series so that the intrinsic viscosities could be determined with reasonable confidence. Another series for No. 397 also was studied at 12.5° to test the effect of solvent viscosity and temperature on the non-Newtonian behavior of rigid particles.

A representative series of flow curves is shown in Fig. 1 where the rate of shear is plotted against the shearing stress on a double logarithmic scale. As was found previously the non-Newtonian viscosity becomes significant above a critical shearing stress τ_c which in turn depends upon the length and the axial ratio of the rods. In Fig. 2 are shown the Martin's plots[11] at constant shearing stress for PBLG No. 397. The good agreement between the intrinsic viscosities obtained from the present instrument and the Ubbelohde-type viscometer (full circles) at $\tau < \tau_c$ indicates that reasonably precise extrapolation of η_{sp}/c to zero concentration can be achieved even using fairly concentrated solutions.

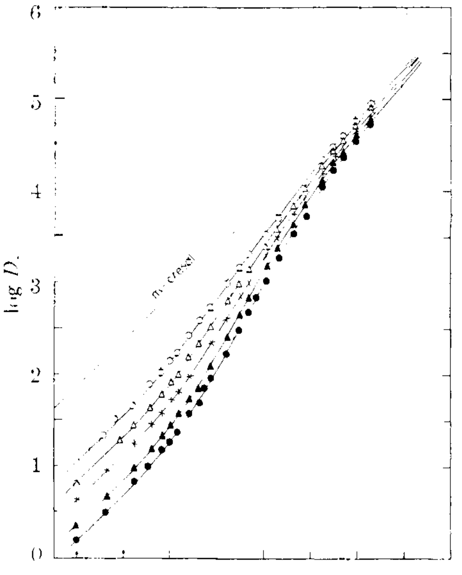

Fig. 1.—Flow curves of PBLG No. 397 in *m*-cresol at 25.0°. The experimental points at $\tau > 10^4$ were omitted in the plot. Concentrations: ○, 0.379%; Δ, 0.502%; ×, 0.621%; ▲, 0.776%; ●, 0.918%.

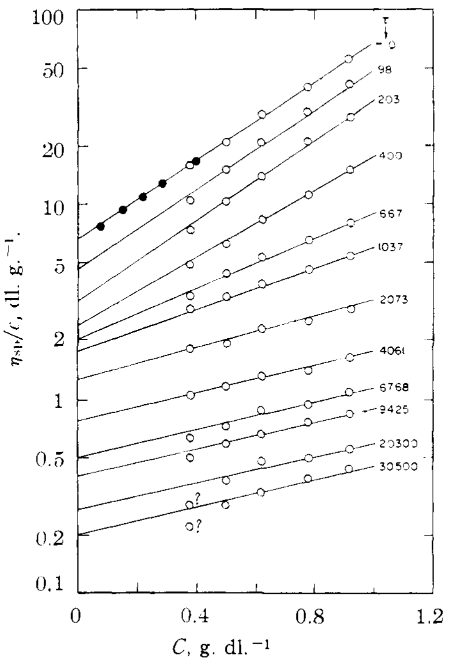

Fig. 2.—Martin's plot of PBLG No. 397 at constant shearing stress: open circles, stainless steel capillary viscometer; closed circles, Ubbelohde viscometer ($\tau < \tau_c$).

Discussion

A. Intrinsic Viscosity as a Function of Shearing Stress.

—According to the viscosity theories of rigid particles[3–5] the ratio of the intrinsic viscosity at finite shear to that at zero shear is given by

$$[\eta]_D/[\eta]_{D=0} = f(\alpha, p) \qquad (7)$$

where p is the axial ratio and α is defined as $\alpha = D/\Theta$, Θ being the rotary diffusion constant of the rod-like particles. From Perrin's equations[12]

$$\eta_0\Theta_b/T = (3k/16\pi a^3)[2 \ln (2a/b) - 1],\ a > 5b \qquad (8a)$$

for prolate ellipsoids, and

$$\eta_0\Theta_a/T = 3k/32b^3,\ b >> a \qquad (8b)$$

for oblate ellipsoids, one finds that $\eta_0\Theta/T$ is a constant characteristic of the macromolecules, independent of either η_0 or T. Here a and b are the semi-major and -minor axes, respectively, η_0 is the solvent viscosity and k and T have the usual meaning. By simple substitution one finds that

$$\alpha = (\tau/T)/(\eta_0\Theta/T) \qquad (9)$$

Thus

$$[\eta]_T/[\eta]_{T=0} = [\eta]_D/[\eta]_{D=0} = F(\tau/T)_p,\ \eta_0\Theta/T = \text{constant} \qquad (10)$$

noting that $\tau = \eta_0 D$ at infinite dilution. By plotting $[\eta]_\tau/[\eta]_{\tau=0}$ against τ/T each system will yield a composite curve which is independent of the solvent and/or temperature used, provided of course there

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[11] A. F. Martin, Abst. 103rd ACS Meeting, April, 1942, p. 1-C; H. M. Spurlin, A. F. Martin and H. G. Tennent, *J. Polymer Sci.*, **1**, 63 (1946).

[12] F. Perrin, *J. phys. radium*, [7] **5**, 497 (1934).

are no configurational changes under the various conditions employed. For this reason, the intrinsic viscosities are plotted as a function of shearing stress (at constant temperature) in Fig. 3.[13]

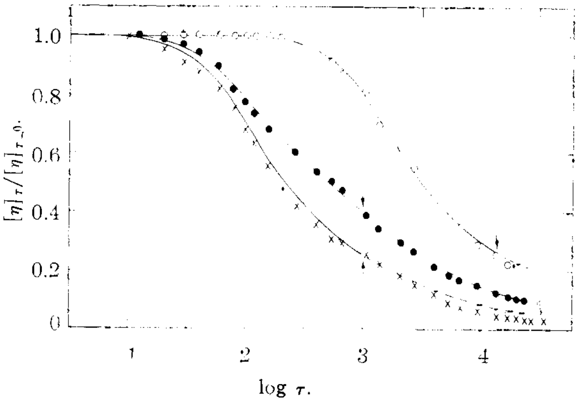

Fig. 3.—Shear dependence of the intrinsic viscosities of PBLG: circles and crosses, experimental values; lines, theoretical curves (broken lines to the right of the arrows, extrapolated curves): curve 1, $\eta_0\Theta/T = 0.76$; curve 3, $\eta_0\Theta/T = 0.054$; curve 2, calculated on the basis of 3 parts curve 1 and 1 part curve 3 (by weight).

The obvious feature in Fig. 3 is the sharp drop in $[\eta]$ with increasing τ. For PBLG No. 397 $[\eta]_\tau$ was reduced from 6.7 at $\tau = 0$ to about 0.2 at the highest attainable shearing stress, whereas for No. 421 it dropped from 1.3 to less than 0.3 in the same range of shearing stress. Previously[2] it was shown that the intrinsic viscosity at high stress of the same polypeptide in the randomly coiled form retained more than 50% of its value at zero stress. The marked difference in the shear dependence of intrinsic viscosity between rod-like particles and flexible coils clearly provides a new means for the study of changes in polymer configurations, as, for example, in protein denaturation.

According to eqs. 8 and 9 the critical stress (when $\alpha \cong 1$) would be expected to be much smaller for longer than for shorter particles since the former have a smaller $\eta_0\Theta/T$. This expectation was indeed fulfilled, as is clearly illustrated in Fig. 3, where PBLG Nos. 421 (curve 1) and 397 (curve 3) have mean $\eta_0\Theta/T$ of 0.76 and 0.054, respectively. From the theoretical calculations[5] the shear dependence of $[\eta]$ appears to be insignificant for $\alpha < 1$. Suppose, now, the common Ubbelohde- or Ostwald-type viscometer has a shearing stress of about ten. It can be shown easily that no non-Newtonian viscosity at, say, 25° will be detected within experimental errors for particles having length (prolate) less than 1900–2900 Å. (for axial ratio, p = 5–300) or diameter (oblate) of about 1500 Å. or less. If the assumed shearing stress is increased by tenfold, the corresponding limits should be reduced to 900–1300 Å. for the prolates and about 700 Å. for the oblates. Thus most of the globular proteins would not exhibit non-Newtonian behavior within experimental errors in the ordinary Ubbelohde- or Ostwald-type viscometers, mainly because the numerical values of $\eta_0\Theta$ are much greater than the applied shearing stress. On the other hand for highly elongated or extremely flattened particles such as tobacco mosaic virus, actomyosin and cellulose crystallites, the shear dependence will be quite appreciable even with the commonly used capillary viscosimeters. If α falls in the regions where the sharp drop in intrinsic viscosity with shear is observed, it is not difficult to see that the customary extrapolation to zero shear by plotting the intrinsic viscosity against the rate of shear would indeed be a very risky and uncertain procedure.

The curves in Fig. 3 were calculated on the basis of weight-average molecular weight from light scattering. PBLG Nos. 421 and 397 (curves 1 and 3) were assumed to have $\eta_0\Theta/T$ values as mentioned above. Curve 2 was obtained by using the well-known relation

$$[\eta] = \Sigma C_i[\eta]_i \qquad (11)$$

for each chosen shearing stress. The good agreement between theory and experimental values in Fig. 3 is self-explanatory and thereby supports the previous conclusions[2] concerning the validity of the viscosity theories for rigid particles and the determination of the rotary diffusion constant from the non-Newtonian viscosity.[14] In fact, the agreement between theory and experiment for PBLG No. 397 is somewhat better than expected because the sample is somewhat polydisperse and because of the unavoidable few per cent. error in the extrapolation in the Martin plots.

B. **Effect of Solvent Viscosity and Temperature.**—To illustrate eq. 10 a series of flow curves of PBLG were also measured in m-cresol at 12.5°, at which temperature the solvent viscosity was more than twice that at 25.0°. As can be seen in Fig. 4 a composite curve of $[\eta]$ *versus* τ/T was indeed obtained as expected. Needless to say, two different curves would have resulted if the intrinsic viscosity had been plotted against the rate of shear. Here is another indication that τ/T or τ (at constant T) appears to be a more logical variable than D for expressing the viscosity behavior of polymers.

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(13) As has been pointed out previously[2] measurements in an Ostwald- or Ubbelohde-type viscometer are made under virtually constant shearing stress since eq. 1 can be re-written as

$$\tau = hdgR/2L$$

where h is the mean hydrostatic pressure head, g the acceleration of gravity and d the density of the solution used, noting that variation of d with concentrations is almost negligible. In the study of shear dependence of viscosity most workers by tradition prefer to express the viscosity as a function of rate of shear. Evidently the latter is not constant in a viscometer and varies inversely with the solution viscosity. It is therefore recommended that the shearing stress rather than the rate of shear be employed in the extrapolation of viscosity to zero shear.

(14) With the determination of the rotary diffusion constant, Θ, from either non-Newtonian viscosity or flow birefringence, one can formulate a relation between the molecular weights, M, of a homologous series of polymers and their $\eta_0\Theta/T$ values. According to eq. 8 oblate ellipsoids (having the same major axis) would yield

$$T/\eta_0\Theta = K_0M^3$$

whereas prolate ellipsoids (having the same minor axis) would have an exponent slightly less than three due to the small variation of the logarithmic term with molecular weight. For the PBLG series we have found that

$$T/\eta_0\Theta = K_pM^{2.82}$$

Here K_0 and K_p are two constants. Thus, in principle one should be able to determine the molecular weights of polymers from a calibration curve, provided $\eta_0\Theta/T$ is known. If the polymer is polydisperse, however, it is difficult to choose the proper Θ values.

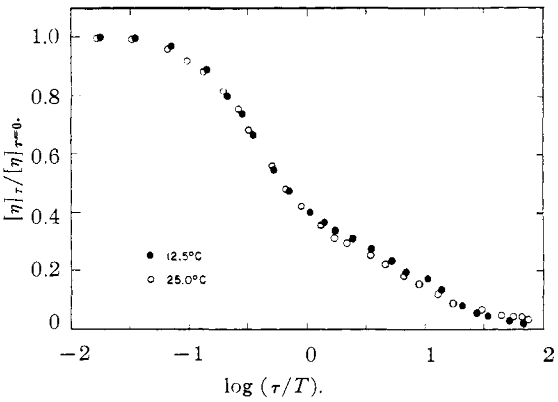

Fig. 4.—Effect of solvent and temperature on the shear dependence of the intrinsic viscosities of PBLG No. 397: closed circles, *m*-cresol at 12.5°; open circles, data taken from Fig. 3.

C. Effect of Polydispersity and the Apparent Length.—Since the longer particles have smaller τ_c values than the shorter particles, it is conceivable that the composite curve of many components in a polydisperse system would result in a broadening of the non-Newtonian region, noting that each component has its characteristic viscosity curve. That this is so is clearly illustrated in Fig. 3, where curve 2 is flatter than either of curves 1 and 3. To pursue this point further we have calculated the intrinsic viscosities as a function of τ/T for a Gaussian and a most probable distribution[15,16] through graphic integrations of eq. 11 and by assuming a mean length L_w of 1800 Å. As is shown in Fig. 5, both calculated curves spread over a wider non-Newtonian region. Furthermore, they lie lower than the curve for a monodisperse system having a length equal to L_w, in exactly the same manner as the extinction angle of the flow birefringence of a polydisperse system.[18] In both cases the apparent rotary diffusion constant Θ at any chosen shear for a polydisperse system is always smaller than that corresponding to L_w. The reason is simply that at low shear the longer particles are more easily oriented, thus yielding a smaller apparent Θ. As the shear increases, even the shorter particles become oriented and as a consequence the apparent Θ gradually increases. Finally as the shear approaches infinity the viscosity curve approaches that for a monodisperse system having the length L_w and the mean Θ results.

In Table II are listed the apparent lengths at several shearing stresses for the most probable distribu-

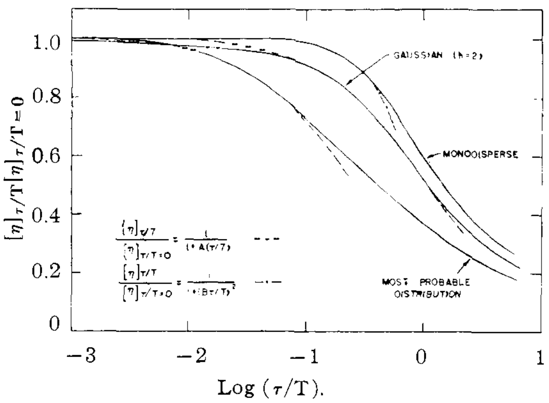

Fig. 5.—Shear dependence of the intrinsic viscosities of rods obeying hypothetic molecular weight distributions.

tion curve in Fig. 5, as calculated by the method described previously.[2] As is expected the apparent length decreases with increasing shear (with the exception of $\tau = 0$), since the apparent Θ is smaller at lower shear. Thus, like flow birefringence the shear dependence of viscosity is another sensitive method for the detection of polydispersity of rigid particles. The seeming paradox at $\tau = 0$, where the mean length is smaller than that at $\tau = 0$, can be explained as follows: as the shear approaches zero the viscosity of the solution is entirely affected by the Brownian motion of the particles. The mean length therefore can be calculated with the aid of eq. 11 for $\tau = 0$. As soon as the shear increases, however, the orientation effect becomes significant for the longer particles, resulting in a drop in viscosity and thereby a sharp increase in the calculated apparent length. Thus in an L_{app}–τ plot the extrapolated length may approach the upper limit of the longest particles but definitely does not represent the mean length at zero shear. The same argument can be applied just as well to the flow birefringence lengths. In Table II it is also noted that the length at $\tau = 0$ as calculated from the intrinsic viscosity was slightly higher than L_w. This is due to the fact that for polymers having the most probable distribution the ratio of M_v (viscosity–average molecular weight) to M_w is equal to $[(1 + a)\Gamma(1 + a)]^{1/a}/2$,[19] where $\Gamma(1 + a)$ is the gamma function of $(1 + a)$, and a is the exponent in the viscosity–molecular

TABLE II

APPARENT LENGTHS OF RIGID ELLIPSOIDS OBEYING A MOST PROBABLE DISTRIBUTION

L_w = 1800 Å., $2b$ = 18 Å.

$(\tau/T) \times 10^2$	Lengths (= $2a$), Å. (from [η])
0	*2080*
1.11	4760
3.34	4040
11.1	3380
33.4	2860
111	2600
334	2460

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(15) A Gaussian distribution for the weight fraction can be expressed as

$$(h/\pi^{1/2}) \exp[-h^2 (\Delta L/L_0)^2]$$

where $\Delta L = L - L_0$, L is the length of the particle, L_0 the mean length and h is a constant which determines the spread of the distribution. In our calculations we have taken $L_0 = L_w = 1800$ Å.

(16) The weight-average degree of polymerization $\bar{X}_w$ and the weight fraction W_x of a most probable distribution are given as[17]

$$\bar{X}_w = (1 + p)/(1 - p)$$

and

$$W_x = x(1 - p)^2 p^{x-1}$$

where x is the degree of polymerization and p the probability of continuation of the linear chain. In the present case, $\bar{x}_w = 1200$.

(17) See, for example, P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953. Chapter VIII.

(18) H. A. Scheraga, *J. Chem. Phys.*, **19**, 983 (1951).

(19) J. R. Schaefgen and P. J. Flory, THIS JOURNAL, **70**, 2709 (1948).

weight equation

$$[\eta] = KM^{a} \qquad (12)^{20}$$

D. Power Law of Viscosity.—For many years there has existed a controversy on the so-called power law of viscosity.[22] By simple geometric analysis viscosity should be an even function of τ (or D) since it is independent of the direction of τ (or D). The majority of published data, however, suggests an uneven function at low shear values, which contradicts most of the theoretical considerations. From the results in Figs. 3 and 5 one finds that the degree of polydispersity could be at least one of the complicating factors which is responsible for the disagreement between theories and experiments. In Fig. 3, curves 1 and 3, which were virtually parallel to each other, obeyed the power law according to the theory of Saito[3] or Kirkwood.[4] On the other hand, curve 2 spread over a broader non-Newtonian region than either of the other two curves and did not agree with the even function of shear.

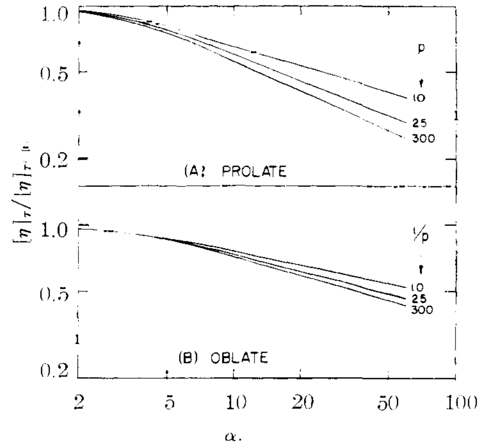

Fig. 6.—$[\eta]_\tau/[\eta]_{\tau=0}$ as a function of α. Theoretical values were taken from ref. 2 and 4, p or $1/p$ being axial ratios.

This deviation is even more evident in Fig. 5, where curves of $y_1 = 1/1+x_1$ and $y_2 = 1/1+x_2^2$ are plotted as y *versus* log x and superimposed on the theoretical curves for different distributions. Clearly both the Gaussian and most probable distributions fit with the first-power law (broken lines) at low shear values with an error of less than 2%. The agreement would be even better if one expresses the power law as

$$[\eta]_\tau/[\eta]_{\tau=0} = 1 - A\tau + B\tau^2 \cdots \qquad (13)$$

On the other hand the monodisperse curve agrees with an even power law as predicted by the theories. Thus for a polydisperse system it is possible to obtain a pseudo-odd function of τ (or D) even though each component obeys an even-power equation. Although this interpretation is aimed at the rigid particles, the same argument is expected to be applicable to flexible chains as well. Furthermore, unavoidable experimental errors can frequently cause agreement with either odd or even function in the low shear ranges. Thus, the current controversy appears to have been overemphasized.

The above controversy has an important implication in the determination of viscosity at zero rate of shear. Many workers prefer to plot η_{sp}/c or $[\eta]$ against the rate of shear and extrapolate it to zero rate of shear although the theories predict an even function of the shear. This procedure may be permissible within experimental errors, although even a straight line from the plot does not necessarily yield a true viscosity at zero shear, as has been pointed out by Eisenberg[23] recently. Needless to say, the situation will be much worse if the η–D plot exhibits an upward curvature as the rate of shear approaches zero.

E. Extension of Theoretical Values.—The numerical solutions of Saito's theory[3] as tabulated by Scheraga[5] were limited to $\alpha = 60$ because of the limited internal storage capacity of the Mark I computer. For most of the experimental measurements this range is more than adequate for the characterization of rigid particles. However, since measurements over a wide range of shear are required to detect and characterize the presence, if any, of polydispersity, it is frequently necessary to extend this limit of α beyond 60. In particular, highly elongated (or flattened) particles would reach the above limit much faster than the shorter ones, even when the applied shear is moderately small. Fortunately, a plot of viscosity increment $\nu^{\prime}$ or the ratio, $[\eta]_\tau/[\eta]_{\tau=0}$ or $[\eta]_D/[\eta]_{D=0}$ *versus* α on a double logarithmic scale was found to yield a straight line at α above five for both prolate and oblate ellipsoids, as can be seen in Fig. 6. Thus the limit of α can be extended by an order of magnitude or two through simple extrapolation. Admittedly this procedure is arbitrary and without theoretical justification and can result in appreciable errors. For the sake of comparison the extinction angle χ of flow birefringence was also plotted against α on a double logarithmic scale, using the published theoretical values.[24] Above $\alpha = 5$ a straight line also resulted (figure not shown). However, a gradual downward curvature appeared between $\alpha = 60$ and 200 (upper limit of the tabulated values), *i.e.*, χ was somewhat smaller than that predicted by the extended straight line for any chosen α. The authors in ref. 24 have pointed out that for $\alpha \leqq 60$ the error of their tabulated values is well under 1%, but for $\alpha \geqq 60$ the listed results are significantly in error for all but very small axial ratios (p), because of the fact that the limiting values of the slowly converging series in their computations have not been reached in the latter cases. In fact, from their Fig. 7 one finds that the calculated extinction angles for $p = \infty$ at $\alpha \geqq 60$ lie significantly lower than the curve shown in the figure, which might account for the apparent downward

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(20) Both a and K in eq. 12 depend on the applied shear. At zero shear, $a \cong 1.7$. When non-Newtonian viscosity becomes significant, a decreases and K increases with increasing shear, mainly because the higher the molecular weight of the polymers the faster the intrinsic viscosity drops with increasing shear. Similar observations have been reported recently by Kuroiwa and co-workers[21] for polystyrene solutions. At very high shear the a values would be expected to rise again since the intrinsic viscosity of lower molecular weight polymers would also drop drastically under these conditions. For PBLG we have found that a reached a minimum of about 0.7.

(21) K. Kawahara, M. Ueda, Y. Oka and T. Kuroiwa, *J. Polymer Sci.*, **31**, 245 (1958).

(22) For a recent brief review, see J. J. Hermans, *Ann. Rev. Phys. Chem.*, **8**, 179 (1957); in particular, p. 185-186.

(23) H. Eisenberg, *J. Polymer Sci.*, **23**, 579 (1957).

(24) H. A. Scheraga, J. T. Edsall and J. O. Gadd, Jr., *J. Chem. Phys.*, **19**, 1101 (1951).

curvature in the log χ–log α plot. Thus it is not certain what deviation, if any, would occur at $\alpha \geqq 60$ and, if so, to what extent it deviates. The same argument can equally be applied to the $[\eta]$–α plot. Therefore it is gratifying to find the good agreement between the experimental points (Fig. 3) and the extended theoretical values (broken lines), thus enabling one to use these extrapolated values with some confidence. The lower experimental values than the calculated ones in curve 3 were at least partly due to the significant experimental errors at high shearing stresses. Similar strikingly good agreement was also found between extrapolated theoretical values and experimental points for PBLG No. 416 in the previous publication[2] even for a 20-fold extension of α (to 1200) (figure not shown here). Nevertheless, the possible uncertainty involved in the extrapolation as mentioned above could be very serious and should be used with reservation unless future experiments indicate otherwise.

NOTE ADDED IN PROOF.—Professor J. J. Hermans has kindly pointed out that the viscosity at the capillary wall, η, can be obtained by straightforward differentiation and represented as

$$1/\eta = (1/\pi R^3\tau^3)\mathrm{d}(Q\tau^3)/\mathrm{d}\tau$$

the symbols having the same meaning as those in eq. 1 and 2 (see also, J. Hermans, Jr., and J. J. Hermans, *Proc. Koninkl. Ned. Akad. Wetenschap.*, **B61,** 324 (1958)). It can be shown that the above equation also yields eq. 3 but without assuming a power law (eq. 6). Thus eq. 3 becomes perfectly exact. In a recent note Reichmann (*J. Phys. Chem.*, **63,** 638 (1959)) has also discussed the effect of polydispersity on non-Newtonian viscosity. Philippoff and Gaskins (*ibid.*, **63,** 985 (1959)) have reinterpreted the author's earlier data (ref. 2) in the light of the power law of viscosity.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Structure of the Cyclic Tetramer of Dimethylgallium Hydroxide[1]

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The monoclinic unit of structure of dimethylgallium hydroxide has $a = 8.62 \pm 0.01$, $b = 12.14 \pm 0.04$, $c = 8.50 \pm 0.02$ Å., $\beta = 92.05 \pm 0.10°$, $P2_1/c$ as space group, and contains $8\mathrm{Me_2GaOH}$. Patterson, Fourier and difference syntheses of photographically recorded X-ray intensity data from the three principal zones of reflection lead to determination of structure. The characteristic species in the crystal is the cyclic tetramer (Fig. 3) of $\bar{1}$ symmetry with hydroxyl oxygen and gallium atoms forming an eight-membered central ring. Averaged values of bond lengths are GaO = 1.96, GaC = 1.97 Å. and of bond angles are OGaO = 98.8, GaOGa = 133.1, CGaC = 129.2, CGaO = 106.2°. The compact molecules pack together closely in the crystal.

Introduction

Kenney and Laubengayer[2] prepared dimethylgallium hydroxide as monoclinic crystals soluble in a variety of organic solvents and melting with accompanying slow decomposition at 87 to 88.5°. Cryoscopic and dipole moment measurements on benzene solutions led to the trimeric formula $(\mathrm{Me_2GaOH})_3$ and a moment of 1.8 debyes for the solute molecule. Both in solution (cyclohexane, carbon tetrachloride) and in a Nujol mull, the compound showed strong infrared absorption bands attributable to OH. These data led the authors[2] to postulate the cyclic trimer with gallium and hydroxyl oxygen atoms alternating around a central six-membered ring as the characteristic species in solution and probably also in the crystal. The related but thermally more stable compounds $(\mathrm{Me_2GaXMe})_n$, in which X = O, S, Se, were found[3] to be dimeric in the vapor phase and were assigned[3] a structure with Ga and X atoms alternating about a central four-membered ring.

The X-ray diffraction study now reported shows that the characteristic molecular species in crystalline dimethylgallium hydroxide is in fact the cyclic tetramer of Fig. 3.

Experimental

Slow evaporation of cyclohexane solutions of purified dimethylgallium hydroxide, kindly furnished by Dr. Kenney,[2] gave well-developed crystals having the aspect of rhomboidal plates. When exposed to the atmosphere the initially colorless crystals slowly developed a white coating insoluble in cyclohexane. The useful life of all specimens used for X-ray study was prolonged by means of a protective coating of polyisobutylene.

All X-ray data were photographically recorded using Cu Kα radiation filtered through nickel foil. The unit cell data are as follows: diffraction symmetry, 2/m; lattice constants, $a = 8.62 \pm 0.01$, $b = 12.14 \pm 0.04$, $c = 8.50 \pm 0.02$ Å., $\beta = 92.05 \pm 0.10°$; density, measured[2] as 1.75 g./cc., calculated as 1.74 g./cc. assuming eight monomeric molecules within the cell; space group, $P2_1/c$. The presence of a few weak reflections forbidden by the glide plane was in all cases convincingly explained[4] in terms of double reflection,[5] and the subsequent structure analysis was in all details compatible with the space group $P2_1/c$.

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[1] Supported in part by National Science Foundation Research Grant NSF-G5924.

[2] M. E. Kenney and A. W. Laubengayer, THIS JOURNAL, **76,** 4839 (1954).

[3] G. E. Coates and R. G. Hayter, *J. Chem. Soc.*, 2519 (1953).

[4] For details of this analysis see Gordon S. Smith, "The Crystal Structure of the Cyclic Tetramer of Dimethylgallium Hydroxide," Cornell University Thesis, Cornell University Library, 1957.

[5] M. Z. Renninger, *Z. Krist.*, **97,** 95 (1937); *Z. Physik*, **106,** 147 (1937).