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

Non-Newtonian Viscosity of Poly-γ-benzyl-L-glutamate Solutions[1]

BY JEN TSI YANG

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The viscosity of a poly-γ-benzyl-L-glutamate sample ($M_w = 208{,}000$; $M_w/M_n = 1.3$) was measured as a function of shearing stress, τ (up to 10^5 dynes cm.$^{-2}$), in solutions in which the polypeptide exists either as rod-like α-helices (*m*-cresol) or as random coils (dichloroacetic acid). The non-Newtonian behavior above a critical τ was markedly affected by the configuration of the polypeptide. At the highest attainable τ the intrinsic viscosity of the rod form was less than $^1/_{10}$ of its value at $\tau = 0$, whereas the coil form under the same conditions retained more than 50% of its $\tau = 0$ viscosity. The theories of Kuhn and Kuhn, Kirkwood and co-workers and Saito for rigid rods or ellipsoids have been confirmed. A new method for determining the rotary diffusion constant and thereby the length of the rigid particles was thus developed. The curves relating η_{sp} and τ for the two forms at comparable concentrations crossed each other, indicating that the helices did not collapse under high stresses. The degree of polydispersity caused a broadening of the non-Newtonian region with respect to τ.

Introduction

The theory of non-Newtonian viscosity for ellipsoidal particles was first explicitly stated by Kuhn and Kuhn,[2] using Jeffery's hydrodynamic treatment[3] and Peterlin's distribution function.[4] It was developed later with more precision by Saito[5] using the same model, and also by Kirkwood and his co-workers[6a,b] for rod-like particles. This problem has been fundamentally solved, since the equivalence of the three theories has been demonstrated by Saito and Sugita.[7] Precise numerical solutions of Saito's equations have now been computed by Scheraga[8] in the same manner as that carried out previously for flow birefringence.[9] As a result the intrinsic viscosity of rigid particles can be evaluated as a function of axial ratio, *p*, and a parameter α ($\alpha = D/\Theta$, D being the rate of shear and Θ the rotary diffusion constant), thus providing a new method for the study of the configuration of rigid particles in dilute solutions. As far as the author is aware, very few experiments, either using unextrapolated data (to zero concentration)[10] or covering a narrow range of D,[11] have been reported to test the validity of this theory for rigid particles.

The dependence of viscosity of random coils on the rate of shear is a more complicated subject. In addition to hydrodynamic orientation which is opposed by Brownian motion, the flexible chains also undergo deformation when subjected to shearing stress. Kirkwood has developed a rigorous general theory of viscosity.[6a,12] However, since the dependence of molecular configuration upon rate of shear is not known explicitly for flexible coils, only the undeformed equilibrium configuration was used, leading to Newtonian viscosity. Theoretical treatment by Rouse[13] and Zimm[14] using a free-draining model has yielded the result that the intrinsic viscosity of random coils is independent of the rate of shear. This, however, is not in accord with existing experimental findings. On the other hand, Bueche[15] using apparently the same model has obtained a dependence of viscosity on rate of shear. The reason for this discrepancy has been discussed recently by Peterlin and Čopič[16] who speculated that Bueche has neglected the compensating effects of deformation and rotation of the coils. Pao[17] using the same types of equations as Rouse has found that in the general case there is a dependence of viscosity on rate of shear unless all the relaxation times of the coils have nearly the same value. Very recently Zimm[18] has indicated that a more general treatment of his theory would also result in a drop in intrinsic viscosity with increasing rate of shear. Since at the present time theory cannot unequivocally predict the extent of this dependence, its elucidation will have to come from further experimental study.

In this paper an experimental study of the non-Newtonian viscosity of both rigid particles and flexible chains will be described. Poly-γ-benzyl-L-glutamate (PBLG) was chosen as a "model" system for two reasons. First, almost all synthetic polymers are polydisperse, which from an experimental point of view poses a serious obstacle in testing any theoretical predictions. PBLG, however, appears to be one of the few polymers which approach the ideal state of monodispersity, as evidenced by light scattering[19] and osmotic pressure[20] studies. Secondly, the molecular properties of this polymer have been well characterized.[19] The molecules exist as rigid, rod-like α-helices[21] in solvents, *e.g.*, *m*-cresol, and as solvated random coils in good solvents, *e.g.*, dichloroacetic acid (DCA).

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(1) Presented at the 132nd American Chemical Society Meeting, New York, September, 1957.

(2) W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **28**, 97 (1945).

(3) G. B. Jeffery, *Proc. Roy. Soc.* (*London*), **A102**, 16 (1922–1923).

(4) A. Peterlin, *Z. Physik*, **111**, 232 (1938).

(5) N. Saito, *J. Phys. Soc. Japan*, **6**, 297 (1951).

(6) (a) 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); (b) J. Riseman and J. G. Kirkwood, in F. R. Eirich, Ed., "Rheology, Theory and Applications," Vol. I, Academic Press, Inc., New York, N. Y., 1956, p. 495.

(7) N. Saito and M. Sugita, *J. Phys. Soc. Japan*, **7**, 554 (1952).

(8) H. S. Scheraga, *J. Chem. Phys.*, **23**, 1526 (1955).

(9) H. A. Scheraga, J. T. Edsall and J. O. Gadd, Jr., *ibid.*, **19**, 1101 (1951).

(10) F. E. Helders and J. D. Ferry, *J. Phys. Chem.*, **60**, 1536 (1956); J. D. Ferry and F. E. Helders, *Biochim. Biophys. Acta*, **23**, 569 (1957).

(11) E. Wada, *J. Sci. Res. Inst.*, **47**, 168 (1953); *J. Polymer Sci.*, **14**, 305 (1954).

(12) J. G. Kirkwood, *J. Polymer Sci.*, **12**, 1 (1954).

(13) P. E. Rouse, Jr., *J. Chem. Phys.*, **21**, 1272 (1955).

(14) B. H. Zimm, *ibid.*, **24**, 269 (1956).

(15) F. Bueche, *ibid.*, **22**, 1570 (1954).

(16) A. Peterlin and M. Čopič, *J. Appl. Phys.*, **27**, 434 (1956).

(17) Y. H. Pao, *J. Chem. Phys.*, **25**, 1294 (1956); unpublished work, presented at the American Physical Society Meeting, Philadelphia, March, 1957.

(18) B. H. Zimm, private communication.

(19) 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).

(20) P. Doty and J. T. Yang, in preparation.

(21) L. Pauling, R. B. Corey and H. R. Branson, *Proc. Natl. Acad. Sci.*, **37**, 205 (1951); L. Pauling and R. B. Corey, *ibid.*, **37**, 235 (1951).

Thus with this polypeptide it will be possible to distinguish the difference in non-Newtonian viscosity due to configurational changes and at the same time to test the validity of current theories of viscosity.

Experimental Details

A. **Materials.**—The PBLG sample (code no. 416) was a gift of Dr. E. R. Blout and Professor P. Doty. The method of preparation has been published elsewhere.[22] Its molecular weight is M_w = 208,000 and M_n = 160,000[20] and its weight-average length (for rods) is 1430 Å.

The solvents *m*-cresol and dichloroacetic acid (Fisher Scientific Company) were redistilled under vacuum before use.

B. **Viscosity Measurements.**—The flow curves were measured in a stainless steel capillary viscometer the details of which will be published elsewhere. This apparatus has been calibrated against a rotational and a cone-and-plate viscometer over a wide range of shearing stresses and also an Ubbelohde-type glass viscometer at very low rate of shear. The results from these instruments were all in very satisfactory agreement.

1. **Calculation of Viscosity.**—The maximum shearing stress τ at the capillary wall was calculated from the equation

$$\tau = \Delta P \cdot R/2L \qquad (1)$$

where Δp is the applied pressure, and R the radius and L the length of the capillary. The corresponding rate of shear D is calculated from the volume flow rate Q

$$D = 4Q/\pi R^3 \qquad (2)$$

The ratio of τ to D gives the viscosity η in poises. Equation 2 is valid only for Newtonian flow (η being independent of τ or D). The corrected D is given as

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

where n is defined as d log D/d log τ at any chosen τ or D.[23] In this paper appropriate corrections were applied in the calculation of non-Newtonian viscosities.

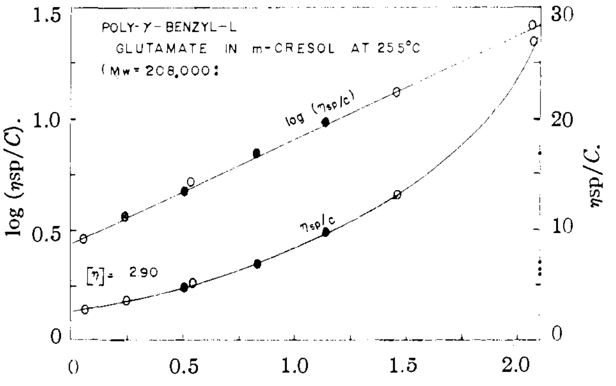

Fig. 1.—Concentration dependence of the reduced viscosities of PBLG No. 416 in *m*-cresol at 25.5°: O, Cannon-Ubbelohde viscometer ($\tau << \tau_c$); ●, stainless steel capillary viscometer (from Fig. 2).

2. **Determination of Intrinsic Viscosity.**—Due to limitations of the instrument the precision of all the measurements was maintained by using fairly concentrated solutions. The intrinsic viscosity $[\eta]$ at constant τ was calculated according to Martin's equation[24]

$$\log (\eta_{\text{sp}}/C) = \log [\eta] + k\,[\eta]C \qquad (4)$$

which is known to hold well for moderately concentrated solutions. This is clearly illustrated in Fig. 1 where a series of the reduced viscosities of PBLG No. 416 at very low rate of shear are plotted according to equation 4 and also according to the well-known Huggins equation. The value of $[\eta]$ in *m*-cresol was found to be 2.90 which was somewhat lower than 3.27 in dimethylformamide and 3.34 in chloroform–formamide,[19] possibly due to the solvent effect on the polypeptide particles. A similar plot for PBLG in DCA gave identical value of $[\eta]$ = 1.19 with that reported in ref. 19, using Huggins' equation. All the intrinsic viscosities in this paper were determined at constant shearing stress. Exhaustion of the polypeptide sample made it necessary to measure only two DCA solutions. Fortunately the concentration dependence of η_{sp}/C was much smaller in DCA than in *m*-cresol. For example, at $\tau \rightarrow 0$ the Martin's slope was 0.45 for the rods and 0.10 for the coils, so that the errors involved in the extrapolation to zero concentration of the coil form were accordingly reduced.

Results

In Figs. 2 and 3 are plotted the so-called flow curves (log rate of shear *vs.* log shearing stress) of PBLG No. 416 in the form of rigid rods (in *m*-cresol) and solvated random coils (in DCA). The viscosity appeared to be Newtonian (where the slope equals 1) at low shearing stress τ followed by a distinct drop with increasing stress and approaching another Newtonian region at very high stress. For the sake of convenience each flow curve can thus be arbitrarily divided into three regions and the stress at which the viscosity drops is assigned as the critical τ_c.

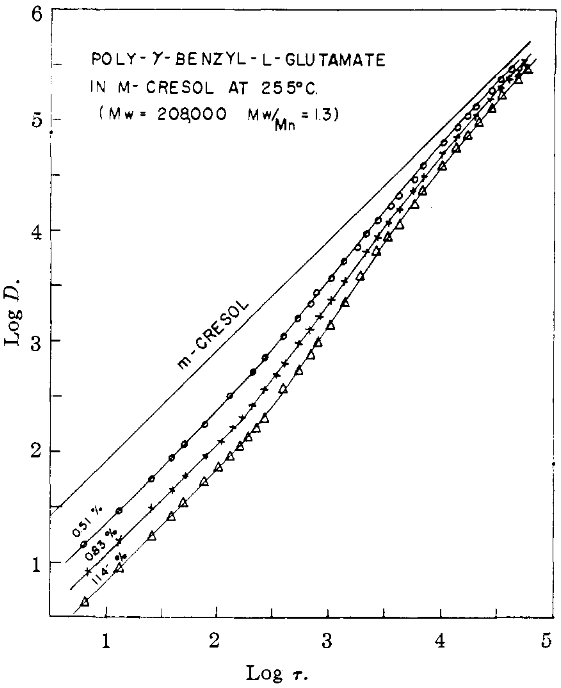

Fig. 2.—Flow curves of PBLG No. 416 in *m*-cresol at 25.5°.

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[22] E. R. Blout, R. H. Karlson, P. Doty and B. Hargitay, THIS JOURNAL, **76**, 4492 (1954); E. R. Blout and R. H. Karlson, *ibid.*, **78**, 941 (1956).

[23] See, for example, M. Reiner, "Deformation and Flow," H. K. Lewis, London, 1949. Equation 3 can also be transformed into

$$\eta_{\text{cor}} = \eta_{\text{ex}}\,(1 + \text{d}\log \eta_{\text{ex}}/\text{d}\log D_{\text{ex}})/[1 + (3/4)\,\text{d}\log \eta_{\text{ex}}/\text{d}\log D_{\text{ex}}] \qquad (3a)$$

where the subscripts refer to experimental and corrected values. Since both τ and D vary along the line perpendicular to the capillary axis, many workers prefer to calculate the mean values of η, τ and D. It seems, however, desirable to use the true τ and D at the capillary wall for the determination of η, as the ratio of mean τ to D does not necessarily yield the corrected η in the non-Newtonian region.

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

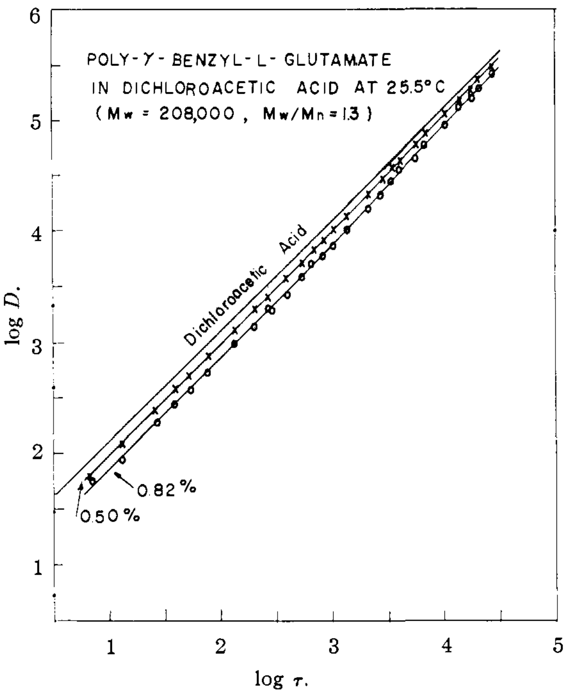

Fig. 3.—Flow curves of PBLG No. 416 in dichloroacetic acid at 25.5°.

Discussions

A. General Considerations.—From the data in Figs. 2 and 3 the reduced viscosities ($= \eta_{sp}/C$) as a function of shearing stress can be calculated and the results are shown in Figs. 4a and 4b. The marked difference in non-Newtonian behavior between rigid rods and random coils is evident. It is noted that the reduced viscosity of the rods dropped to less than one tenth its original value at the highest stress attainable. This was more drastic at higher concentrations. In contrast the reduced viscosity of the coils was only mildly reduced under the same conditions. More striking was the fact that the curves for the two forms at comparable concentrations crossed each other. Within the range of stress studied the intrinsic viscosity at constant stress $[\eta]_\tau$ of the rods dropped from 2.9 to about 0.2, whereas that of the coils dropped only from 1.2 to about 0.8. One is therefore led to believe that the α-helices remain stable even when subjected to the prevailing shearing stress (up to 5 × 10^4 dynes cm.$^{-2}$). Indeed the above result would have been inconceivable (even with due consideration of the solvent effects), if the intramolecular hydrogen bonds stabilizing the rod form had given way under stress. Strong evidence against any configurational change of the helices came also from the close agreement between theory and experiment for rod-shaped molecules as will be discussed in a later section. This confirmation of the theoretical prediction would be impossible if the rod form collapsed under external forces.

Two other interesting features became apparent from the flow curves. First, the non-Newtonian viscosity became significant above a certain critical stress τ_c irrespective of concentration[25] or temperature[26] (within the ranges studied). The corre-

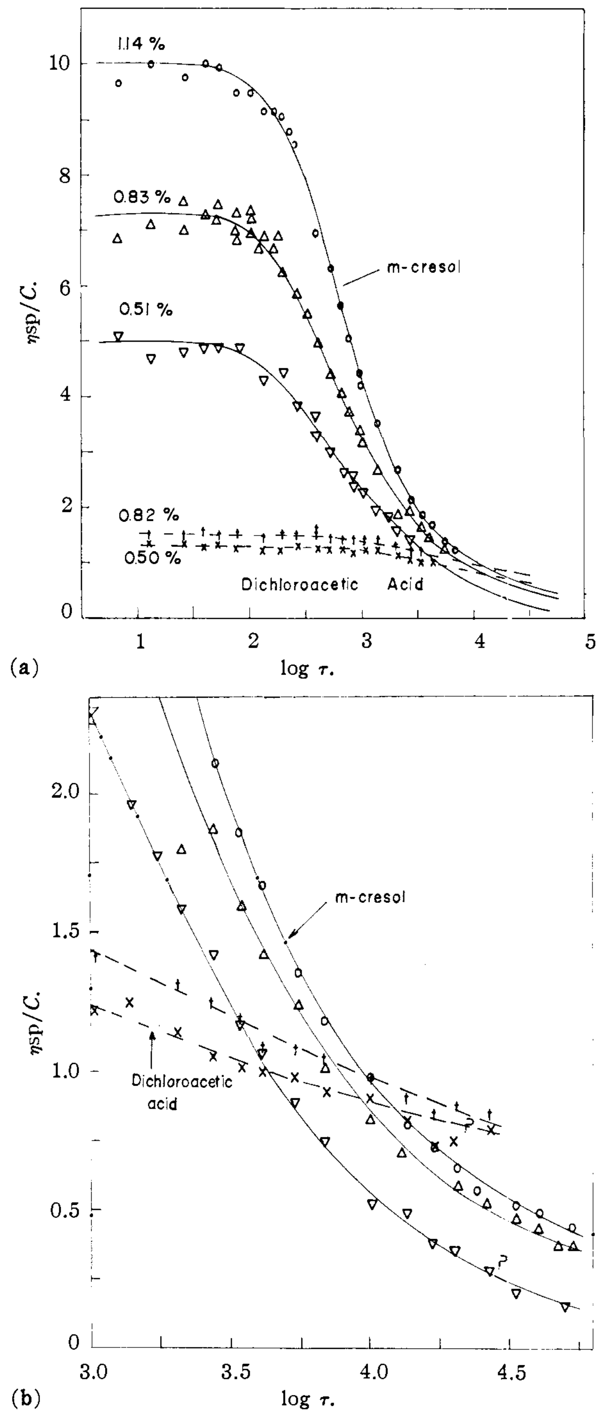

Fig. 4.—Reduced viscosities of PBLG No. 416 as a function of shearing stress. Data taken from Figs. 2 and 3. (b) is a portion of (a) on an enlarged scale.

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[25] In the literature τ_0 of many polymers have been reported to increase gradually with increasing concentration. See, for example, W. Philippoff, "Viskositat der Kolloide," Dresden, 1942. Whether the polypeptide concentration in our studies was not high enough to show such difference or the polydispersity of those polymers caused such variation still awaits further investigations.

[26] The flow curves of a 0.51% PBLG solution in *m*-cresol were measured at 15, 25 and 35° (data not shown here). Those of another 0.54% solution were determined in an Ubbelohde viscometer from 25 to 81° at shearing stress well below τ_c. The activation energy for flow, ΔE^*, was about 10 kcal. as compared with 8.6 kcal. for the solvent. Slow degradation of the polypeptide began at temperatures above 80° as indicated by gradual drop in viscosity on standing.

sponding rate of shear D_c varied inversely with the concentration. This variation usually extended to several orders of magnitude.[25] Thus the shearing stress appears to be a better parameter than the rate of shear in the characterization of non-Newtonian viscosity. It is interesting to note that in an Ostwald- or Ubbelohde-type viscometer measurements are actually made under constant stress rather than constant rate of shear, since the average hydrostatic pressure head is kept virtually constant.

Secondly, in the case of rigid particles, the non-Newtonian region covered about two to three decades of shearing stress, which as will be shown later agreed well with the theoretical prediction for a rigid rod. For polydisperse systems this region usually extended to more than four or five decades.[25] Since each component has its characteristic non-Newtonian behavior the composite curve of many components would conceivably result in a spreading of the non-Newtonian region. Thus some indication of the degree of polydispersity can be obtained from the shape of the curves.

B. Viscosity of Rigid Rods.—The viscosity increment ν as a function of α $(= D/\Theta)$ for various axial ratios p has been tabulated by Scheraga.[8] ν, in turn, can be converted into the conventional intrinsic viscosity $[\eta]$ by the relation

$$[\eta] = \lim_{C \to 0} \frac{\eta - \eta_0}{\eta_0 C} = N V_e \nu / 100 M \qquad (5)$$

where η and η_0 are the viscosities of solution and solvent, N is Avogadro's number, V_e and M are the equivalent hydrodynamic volume and molecular weight of the solute and $[\eta]$ is expressed in dl. per g. At any rate of shear (noting that $D = \tau/\eta_0$) $[\eta]_D/[\eta]_{D=0}$ is simply equal to $\nu_D/\nu_{D=0}$. (Numerical values of these ratios are listed in the Appendix.) In Fig. 5 is shown the dependence of $[\eta]_D$ on D for both the rod and coil forms. The solid line for rods represented a theoretical curve for PBLG No. 416 (Θ = 500 sec.$^{-1}$) in *m*-cresol. Evidently the agreement between theory and experiments (open circles) was as good as could be expected. In fact, our data have extended beyond Scheraga's computations (maximum α = 60). It thus appears that the validity of the theory for rigid rods or ellipsoids is completely confirmed. It is noted, however, that the minor degree of polydispersity of the polypeptide could not be detected precisely. These details will be discussed in a future publication.

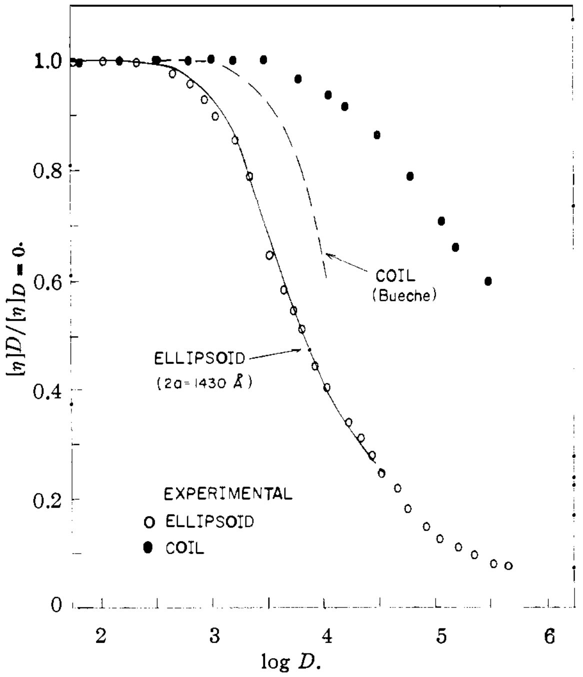

Fig. 5.—$[\eta]D/[\eta]_{D=0}$ as a function of rate of shear: lines, theoretical curves; circles, experimental values.

C. A New Method for Determining the Particle Length.—The agreement between theory and experiments of rigid rods or ellipsoids is indeed gratifying. It leads to a new method for determining the shape of asymmetric particles. Like the flow birefringence technique, it gives a direct measurement of the rotary diffusion constant, Θ.[27] The calculations are also essentially identical with those employed in the flow birefringence method. First, the axial ratio p of the ellipsoid is estimated from $[\eta]_{D=0}$ using Simha's equations for viscosity increment, ν[28,29]

$$\nu = p^2/15\,(\ln 2p - 1.5) + p^2/5\,(\ln 2p - 0.5) + 14/15,\ p >> 1 \qquad (6a)$$

for prolate ellipsoids and

$$\nu = 16p'/15 \text{ arc tan } p',\ p' >> 1 \qquad (6b)$$

for oblate ellipsoids, where $p = a/b$ and $p' = b/a$. Secondly, from the experimental values of $[\eta]_D/[\eta]_{D=0}$, the corresponding α's at constant p can be obtained using Scheraga's tables.[8] For p values other than those listed in the Appendix, the α's can be obtained easily through interpolation or extrapolation. Thirdly, knowing α at any chosen rate of shear, one can immediately calculate Θ $(= D/\alpha)$ and thereby the linear dimension of the particles according to Perrin's equations.[31]

$$\Theta_b = (3kT/16\pi\eta_0 a^3)[2 \ln (2a/b) - 1],\ a > 5b \qquad (7a)$$

for prolate ellipsoids and

$$\Theta_a = 3kT/32\eta_0 b^3,\ b >> a \qquad (7b)$$

for oblate ellipsoids, where a and b are the semi-major and semi-minor axes, k is Boltzmann's constant, T the absolute temperature and η_0 the solvent viscosity.

This method has an additional advantage in its applicability to colored solutions, which are usually difficult to study with physical methods involving optical arrangements. In principle it also enables one to determine the molecular weight distribution of the system by comparing the experimental results with the theoretical curves for systems having

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(27) The relaxation time τ_a for rotation of the major axis a can be calculated from Θ_b about the minor axis b, by the simple reciprocal relation $\tau_a = 1/2\Theta_b$. For PBLG No. 416 in *m*-cresol τ_a was found to be 1×10^{-3} sec.

(28) R. Simha, *J. Phys. Chem.*, **44**, 25 (1940); J. W. Mehl, J. L. Oncley and R. Simha, *Science*, **92**, 132 (1940).

(29) According to equation 5, $[\eta]$ depends on both ν and V_e.[30] However, as an approximation one can assume that the partial specific volume $\bar{V}$ of the solute equals NV_e/M. As can be seen in the Appendix a small variation in p will not affect $[\eta]_D/[\eta]_{D=0}$ as a function of α significantly.

(30) H. A. Scheraga and L. Mandelkern, THIS JOURNAL, **75**, 179 (1953).

(31) F. Perrin, *J. Phys. Radium*, [7] **5**, 497 (1934).

a known distribution function. One drawback of this method is the limited precision of the instrument which makes it difficult to study very dilute solutions, thus causing possible complication in the extrapolation of η_{sp}/C to zero concentration.[32] However, the present apparatus was so designed that it covered as wide a range of shearing stresses as possible. A more elaborate and sensitive instrument covering a smaller range of stresses can be built to yield more precise viscosity measurements. Furthermore, since Θ is, as a first approximation, inversely proportional to the cube of the length, the error involved in the estimation of the length is only one third of that in the measurement of Θ.

For particles having low asymmetry and thereby large θ in a given medium the non-Newtonian viscosity will occur only at very high τ_c (and D_c). In such cases θ can be reduced by increasing the solvent viscosity through the use of an additive such as glycerol or by lowering the solution temperature. This practice is well-known for slow birefringence measurements. It is noted, however, that τ_c of a particular system is independent of solvent viscosity and is also little affected by small changes in temperature,[33] provided, of course, there is no configurational change under these conditions.

Appendix

TABLE I

$[\eta]D/[\eta]_{D=0}$ OF PROLATE ELLIPSOIDS AS A FUNCTION OF α $(= D/\Theta)$ FOR VARIOUS AXIAL RATIOS $p^{a,b,c}$

α / $p \rightarrow$	4	10	16	20	25	50	100	300
0.00	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
.25	0.9996	0.9993	0.9989	0.9990	0.9989	0.9989	0.9988	0.9988
.50	.9979	.9971	.9960	.9959	.9958	.9955	.9955	.9956
.75	.9953	.9927	.9912	.9909	.9908	.9904	.9899	.9897
1.00	.9916	.9868	.9846	.9839	.9837	.9830	.9823	.9820
1.25	.9874	.9787	.9765	.9756	.9750	.9734	.9729	.9724
1.50	.9820	.9707	.9669	.9657	.9649	.9632	.9619	.9612
1.75	.9762	.9604	.9559	.9546	.9534	.9508	.9496	.9486
2.00	.9698	.9501	.9441	.9424	.9409	.9378	.9362	.9348
2.25	.9629	.9391	.9316	.9294	.9277	.9242	.9220	.9203
2.50	.9558	.9274	.9187	.9159	.9139	.9095	.9070	.9051
3.00	.9408	.9032	.8918	.8881	.8853	.8795	.8764	.8736
3.50	.9256	.8782	.8642	.8599	.8563	.8490	.8452	.8418
4.00	.9106	.8540	.8378	.8323	.8281	.8196	.8149	.8109
4.50	.8962	.8305	.8120	.8059	.8011	.7913	.7859	.7813
5.00	.8825	.8092	.7877	.7810	.7755	.7647	.7585	.7532
6.00	.8576	.7689	.7439	.7358	.7291	.7161	.7091	.7027
7.00	.8357	.7344	.7060	.6966	.6893	.6742	.6665	.6595
8.00	.8171	.7049	.6733	.6631	.6548	.6386	.6300	.6223
9.00	.8008	.6792	.6450	.6338	.6251	.6080	.5985	.5905
10.00	.7866	.6566	.6203	.6086	.5992	.5809	.5712	.5628
12.50	.7583	.6113	.5706	.5575	.5474	.5271	.5166	.5074
15.00	.7367	.5747	.5305	.5165	.5053	.4838	.4728	.4634
17.50	.7208	.5500	.5037	.4890	.4773	.4549	.4435	.4338
20.00	.7077	.5282	.4801	.4646	.4526	.4295	.4177	.4080
22.50	.6970	.5104	.4606	.4446	.4323	.4088	.3970	.3872
25.00	.6880	.4949	.4437	.4275	.4149	.3910	.3790	.3692
30.00	.6738	.4700	.4165	.3997	.3868	.3623	.3502	.3405
35.00	.6631	.4503	.3951	.3779	.3646	.3416	.3276	.3181
40.00	.6547	.4342	.3779	.3600	.3464	.3213	.3093	.2998
45.00	.6479	.4203	.3623	.3442	.3305	.3051	.2931	.2837
50.00	.6429	.4079	.3487	.3304	.3164	.2907	.2788	.2697
60.00	.6337	.3872	.3254	.3065	.2921	.2661	.2543	.2454

[a] Calculated from the data in ref. 8. [b] $p = a/b$, where a = semi-major axis and b = semi-minor axis. [c] $\alpha = D/\Theta$, where D = rate of shear and Θ = rotary diffusion constant.

D. Viscosity of Random Coils.—The experimental data for random coils in Fig. 5 should be considered with reservations. Due to limitations of the instrument, the calculated η_{sp}/C values were unavoidably scattered, especially since the solution viscosity was only 1.5 to 2.5 times that of the solvent. Since only two concentrations were studied it was necessary to determine the intrinsic viscosities from the smoothed flow curves. One of the

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(32) Likewise the uncertainty involved in the interpretation of flow birefringence data at finite concentrations raises some doubt about its applicability.

(33) It can be shown easily that as concentration approaches zero

$$\tau_{c_1}/\tau_{c_0} = T_1/T_0$$

irrespective of solvent viscosity. Here τ_{c0} and τ_0 are the critical values in different solvent media or in the same solvent at two temperatures T_0 and T_1.

TABLE II

$[\eta]_D/[\eta]_{D=0}$ OF OBLATE ELLIPSOIDS AS A FUNCTION OF $\alpha(= D/\Theta)$ FOR VARIOUS AXIAL RATIOS $1/p$[a]

α $1/p \rightarrow$	10	25	50	100	300
0.00	1.0000	1.0000	1.0000	1.0000	1.0000
.25	0.9995	0.9995	0.9992	0.9994	0.9995
.50	.9978	.9978	.9972	.9973	.9971
.75	.9949	.9945	.9940	.9939	.9937
1.00	.9911	.9901	.9895	.9893	.9893
1.25	.9863	.9846	.9838	.9837	.9834
1.50	.9806	.9786	.9773	.9770	.9766
1.75	.9744	.9714	.9699	.9695	.9693
2.00	.9674	.9632	.9619	.9612	.9610
2.25	.9601	.9549	.9531	.9525	.9517
2.50	.9524	.9467	.9443	.9433	.9424
3.00	.9363	.9285	.9255	.9243	.9234
3.50	.9199	.9098	.9064	.9049	.9039
4.00	.9038	.8917	.8877	.8857	.8843
4.50	.8882	.8741	.8695	.8672	.8658
5.00	.8733	.8576	.8521	.8495	.8477
6.00	.8458	.8268	.8203	.8171	.8150
7.00	.8216	.7993	.7921	.7884	.7858
8.00	.8002	.7757	.7671	.7631	.7604
9.00	.7813	.7544	.7452	.7408	.7379
10.00	.7645	.7356	.7255	.7210	.7179
12.50	.7296	.6960	.6849	.6796	.6759
15.00	.7007	.6636	.6510	.6450	.6408
17.50	.6799	.6399	.6266	.6203	.6159
20.00	.6613	.6190	.6050	.5981	.5935
22.50	.6455	.6009	.5865	.5793	.5744
25.00	.6315	.5849	.5697	.5624	.5573
30.00	.6084	.5580	.5421	.5342	.5290
35.00	.5895	.5362	.5188	.5111	.5056
40.00	.5734	.5174	.4997	.4912	.4860
45.00	.5596	.5010	.4827	.4740	.4686
50.00	.5474	.4862	.4673	.4582	.4526
60.00	.5272	.4613	.4411	.4316	.4258

[a] See the footnotes in Table I.

main purposes of this paper was, however, to show clearly the difference in non-Newtonian behavior between rigid rods and random coils rather than to present the precise $[\eta]$ values of the coils. Nevertheless, it is reasonably certain that with increasing shearing stress the coils retained one-half of their $[\eta]_{D=0}$ value under the conditions employed. Furthermore, the $[\eta]_D/[\eta]_{D=0}$ ratios appeared to level off gradually at the highest attainable shearing stresses.

As has been mentioned earlier, the theories for random coils are still controversial. Our results in Figs. 3, 4 and 5 clearly indicate a drop in $[\eta]$ with increasing shearing stress, which does not agree with the theories of Kirkwood, Rouse and Zimm. On the other hand, Bueche's theory for free draining coils predicts a drastic decrease in $[\eta]$ as a function of $D\tau_1$[34] (Fig. 5) which is also not in accord with our experimental data. To account for the dependence of $[\eta]$ on rate of shear Zimm[14] has suggested that the non-Gaussian behavior or the stiffness of polymer chains could result in a deviation from the ideal case where rotations between chain segments are completely free. Some experimental evidence in support of Zimm's explanation can be found in the recent work by Philippoff[35] and Kuroiwa.[36] The estimated $[\eta]_{D=\infty}/[\eta]_{D=0}$ of a polyisobutylene (mol. wt. $\approx 10^6$) from Philippoff's data was about 1/1.6. In the second case $[\eta]$ of one polystyrene fraction (mol. wt. $= 3.2 \times 10^6$) varied from 4.3 at $D = 0$ to 4.0 at $D = 2000$ sec.$^{-1}$, a drop of less than 10%. The $[\eta]$-D curve appeared to level off, even though the range covered was rather limited. These two polymers are considered among the class of highly flexible chains and their intrinsic viscosity was only slightly reduced with increasing rate of shear. The details of the theories of Pao[17] and Zimm[18] are not yet available, so that it is difficult to compare our experimental data with theory.

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MARCUS HOOK, PENNSYLVANIA

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[34] τ_1 may be considered as a characteristic relaxation time of the polymer particles (not to be confused with the symbol for shearing stress τ) and is defined as

$$\tau_1 = 12[\eta]_{D=0}\,\eta_0 M/\pi^2 RT \qquad (8)$$

Here M is the molecular weight of the polymer and η_0 the solvent viscosity. The dimension of $[\eta]_{D=0}$ is ml. g.$^{-1}$ rather than the customary dl. g.$^{-1}$. For PBLG No. 416 τ_1 was found to be 7.61×10^{-5} sec.

[35] W. Philippoff, private communication.

[36] T. Kuroiwa, *Bull. Chem. Soc. Japan*, **29**, 164, 962 (1956).