# *Non-Newtonian Viscosity of Dilute High Polymer Solutions. III. On the Method of Measuring Zero Shear Viscosity*

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## Introduction

It is now recognized that, when molecular weight of a polymer is high enough, the effect of the rate of shear on the solution viscosity is by no means negligible even when working with extremely dilute solutions[1-9]. As the result, various investigators have sought to obtain a method of extrapolating the viscosity data at the finite rate of shear to zero shear rate[2-4,10,11].

Some have proposed the linear extrapolation of logarithm of viscosity vs. rate of shear plot for such a method[2,12]. E. Wada[7] and the present writer[8], however, have found that the viscosity vs. shear rate curve shows an antisigmoidal form having a horizontal tangent at the origin rather than an exponential form. This behavior is in accordance with the theories of Kuhn and Kuhn[13] and Saito[14] according to which the viscosity of a dilute polymer solution should be given by an equation of the form:

$$\eta_{sp}=\eta_{sp0}(1-aq^2+bq^4-\cdots\cdots), \qquad (1)$$

where $\eta_{sp0}$ is $\eta_{sp}$ at zero shear rate, $q$ denotes rate of shear and $a$, $b$, etc. are non-Newtonian parameters. This means that the linearity of such a semi-log plot can not be satisfied at least in low shear rate region. Fig. 1 shows log $\eta_{sp}/c$ vs. $q$ plots for several polystyrene fractions of different molecular weights in toluene by

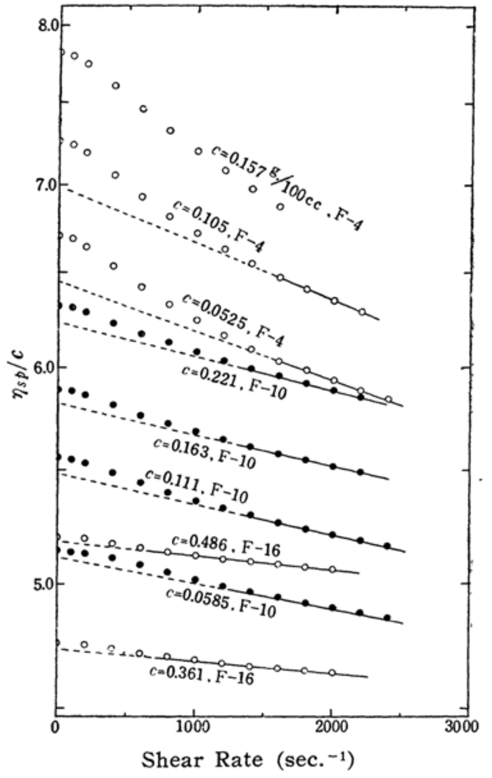

Fig. 1. log $\eta_{sp}/c$ vs. shear rate for polystyrene fractions F-4 ($M_w=4.10\times10^6$), F-10 ($M_w=3.08\times10^6$) and F-16 ($M_w=1.98\times10^6$) in toluene at 25°C.

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[1] C. M. Conrad, V. W. Tripp and T. Mares, *J. Phys. Colloid Chem.*, **55**, 1474 (1951).

[2] T. G. Fox Jr., J. C. Fox, and P. J Flory, *J. Am. Chem. Soc.*, **73**, 1901 (1951).

[3] H. T. Hall and R. M. Fuoss, ibid., **73**, 265 (1951).

[4] G. De Wind and J. J. Hermans, *Rec. trav. chim. Bay-Bas*, **70**, 521, 615 (1951).

[5] F. Akkerman, D. T. F. Pals and J. J. Hermans, ibid., **71**, 56 (1952).

[6] L. S. Sharman, R. H. Sones and L. H. Cragg, *J. Appl. Phys.*, **24**, 703 (1953).

[7] E. Wada, *J. Sci. Research Inst.*, **47**, 149, 159, 168 (1953); *J. Polymer Sci.*, **14**, 305, 307 (1954).

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[9] M. A. Golub, *J. Polymer Sci.*, **18**, 27, 156 (1955); *J. Phys. Chem*, **60**, 431 (1956).

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[11] J. Schurz, ibid., **10**, 123 (1953).

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the experimental data reported in the previous paper[8]*. Evidently, it is not possible to give a fully linear representation to each of these plots over the entire range of shear rate. The plots for the lower molecular weight fractions, however, may be regarded to be linear in the region of higher shear rates and the approximately linear portions of these curves appear to extend towards a low rate of shear as molecular weight of the polymer decreases. Therefore the linear extrapolation of log $\eta_{sp}/c$ in these shear ranges to zero shear will yield a fairly good approximation to the zero shear viscosity when molecular weight of the polymer is not so much high as those of the fractions shown in Fig. 1. Moreover, it seems that the tangent of the linear portion is independent of concentration for a given fraction as pointed out by Fox, Fox and Flory.[2] An upward deviation from linearity of $\ln \eta_r$ vs. $q$ curves at lower shear rates has been observed also by Cragg et al.[6] for polystyrene solutions, although the shear rate at which the deviation commences appears to be higher than in the present case.

Recently, Katchalsky[15] has suggested the method of obtaining the zero shear viscosity making use of the relationship he derived:

$$\frac{t_s}{t}=\frac{\eta_s}{\eta_0}\left(1+\frac{aP^2R^2}{3\eta_0{}^2L^2}\right), \tag{2}$$

where $t$ and $t_s$ are the flow times of the solution and solvent, respectively, at pressure $P$, $\eta_s$ is the viscosity of the solvent and $\eta_0$ the viscosity of the solution at zero shear, $a$ is a non-Newtonian parameter appeared in Eq. (1), $R$ and $L$ the radius and length of the capillary, respectively. According to Eq. (2), if a series of measurements are made in viscometers of different capillary radii at the same pressure, or alternatively, at different pressures in the same viscometer, then the resulting $t_s/t$ vs. $P^2R^2$ plot should be a straight line, and the zero shear viscosity, $\eta_0$, can be determined as the reciprocal of the intercept of this line at the origin multiplied by $\eta_s$. Katchalsky derived Eq. (2) on the basis of the theoretical equation (1). For small shear rate, Eq. (1) reduces to the simpler form:

$$\eta_{sp}=\eta_{sp0}(1-aq^2), \tag{3}$$

and this equation was used in deriving Eq. (2).

For most polymer solutions, however, the shear rate range in which Eq. (3) can adequately describe the shear dependence of solution viscosity appears to be confined to very low shear rates which the ordinary viscosity method by a capillary viscometer can deal with only with difficulty. This opinion may be borne out by the fact that such a quadratic dependence of viscosity has been observed only by a few recent investigators[7,8,16,17] who have extended the measurements down to very low shear rates by the use of a specially designed viscometer. For example, the quadratic range was found to lie below the gradients of about 200–300 sec.$^{-1}$ for those polystyrene fractions in toluene though it depends on concentration and molecular weight of the polymer to some extent (see Fig. 2). Therefore Katchalsky's equation (2) may be expected to hold when measurements are made only at small gradients to which the routine method of viscometry by a capillary viscometer is not easily accessible.

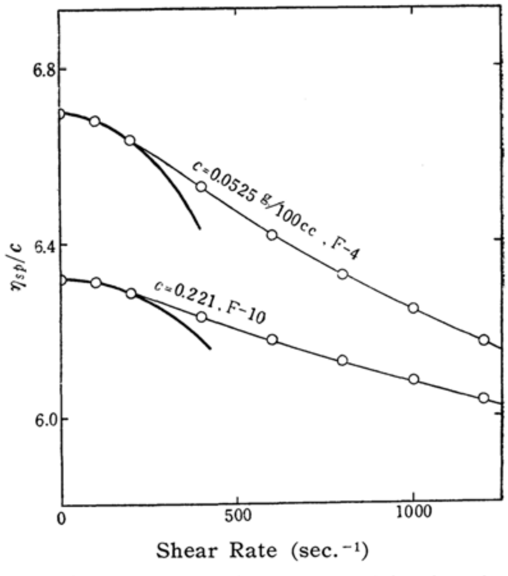

Fig. 2. $\eta_{sp}/c$ vs. shear rate. The heavier line shows the curve according to Eq. (3).

The present writer has examined these previous results on polystyrene in various ways, seeking after an available method for obtaining zero shear viscosity involving nothing more than a straight-line extrapo-

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[*] The shear rate dealt with in the routine method of viscometry of dilute polymer solutions will usually fall in the shear rate range of 500-3000 sec$^{-1}$.

[15] A. Katchalsky and N. Sternberg, *J. Polymer Sci.*, **10**, 253 (1953).

[16] H. Fujita and T. Homma, *J. Polymer Sci.*, **15**, 277 (1955).

[17] P. Alexander and K. A. Stacey, *Trans. Faraday Soc.*, **51**, 299 (1955).

lation, which should hold over a sufficiently wide range of shear rates. But the mathematical relationship between viscosity and shear rate was too complex to warrant generalization and none of these attempts was successful.

Another method of measuring the zero shear viscosity has been proposed by E. Wada7) in which the use of a tilting viscometer is recommended. Taking advantage of a horizontal tangent at very small shear rates in the viscosity vs. shear curve, the apparent relative viscosities are measured at successively low pressures by tilting the viscometer until they begin to assume a constant value, which is substantially the relative viscosity at zero shear.

The present writer has measured the zero shear viscosities of polystyrene fractions in toluene according to the same principle using a multi-bulb viscometer instead of the tilting type and found that the results thus obtained are in good agreement with the zero shear viscosities previously measured by a horizontal viscometer8). In the following, the viscometer is briefly described and the results are compared with the previous results.

## Viscometer

A sketch of the viscometer used is shown in Fig. 3. In order to carry out measurements at sufficiently low rates of shear, the capillary was made small in radius (R=0.0131 cm.) and long (L=30.0 cm.). The upper part of each tube of the viscometer was bent as shown in Fig. 3 so as to allow the viscometer to be inclined at nearly horizontal positions without shedding the charged liquid, which procedure is necessary to fill the liquid in the capillary portions without allowing air to remain in the bent portion between the two capillaries.

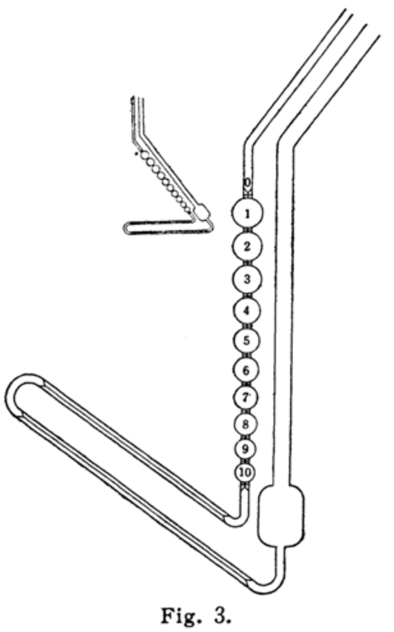

Fig. 3.

Since fairly rapid fall of the liquid in the strait portions at the etched lines (0, 1, 2, 3, etc. in Fig. 3) is desirable for the facility of flow time measurements, and since the flow velocity in this viscometer is very small owing to the long fine capillary, the straits in lower part of the viscometer were made fairly narrow (0.03 cm. in diameter for the lowest at the line 10). These narrow straits not only play a roll of capillary to some extent but also cause the surface tension error when the difference in surface tension between the solution and solvent is appreciable. But for the present case, at least, this error is considered negligible if it exists at all since the results obtained by this viscometer are in good agreement with those by a horizontal viscometer, in which the surface tension effect is almost completely absent. The measurement using the lowest efflux bulb (9-10) was found to be impossible for polystyrene solutions in toluene due to the capillary rise of the solvent in the strait at the line 10, which was absent in measurements of polymethylmethacrylate solutions in chloroform.

The viscometer was fixed on a brass frame, which in turn can be mounted on a frame in a thermostat so as to ensure the reproducibility of the viscometer position, which is very essential to the reliable measurements.

The kinetic energy correction for this viscometer was found to be negligible being consistent with the very small flow velocity in the viscometer. The drainage error was assumed to be also negligible.

## Results

The ratios of the flow times of the solution and solvent, $t/t_0$, for two polystyrene fractions in toluene, measured at 25°C are shown graphically in Figs. 4 and 5 plotted against the mean pressure head, $h$, and shearing stress, $\tau$. Here $\tau$ was calculated according to the equation:

$$\tau=\rho g h R/2L \qquad (4)$$

which is the expression for the maximum shearing stress at the capillary wall, where $\rho$ is the density of the solution. The shear rate ranges covered by these measurements are 54-201 sec.$^{-1}$ for the solution of $c=0.196$ g./100 cc. of F-4, 109-405 sec.$^{-1}$ for $c=0.0568$ of F-10.

As seen in Figs. 4 and 5, $t/t_0$ appears to attain a constant value at lower pressures and this value may be regarded as the $t/t_0$ at zero pressure. In this range of pressures, the linearity of the Katchalsky plot, $t_0/t$ vs. $h^2$, was found to be satisfied very well by these data as may be expected. Though these plots are not shown here, $t/t_0$ at zero shear rate determined from the intercept of the straight line in these plots was substantially coincident with the one provided by

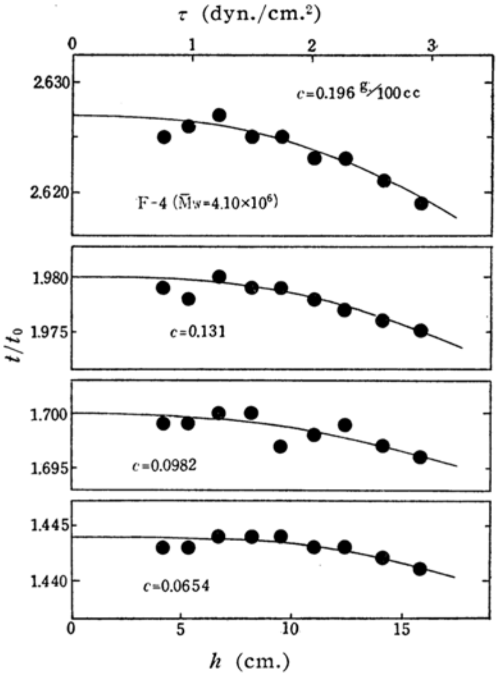

Fig. 4. The ratio of the flow times of the solution and the solvent vs. the mean pressure head, $h$, and shearing stress, $\tau$. See Eq. (4) for $\tau$.

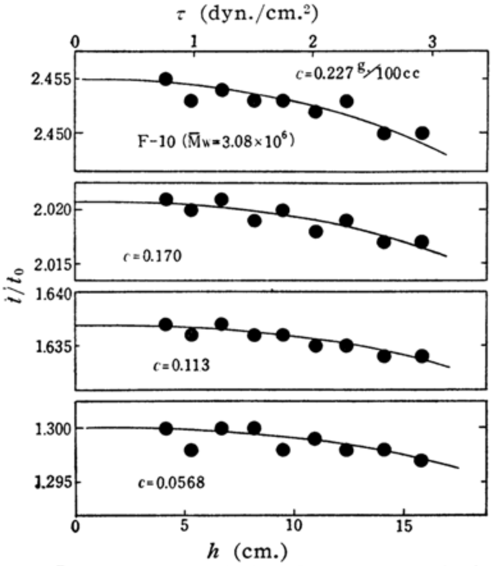

Fig. 5. The ratio of the flow times of the solution and the solvent vs. the mean pressure head, $h$, and shearing stress, $\tau$. See Eq. (4) for $\tau$.

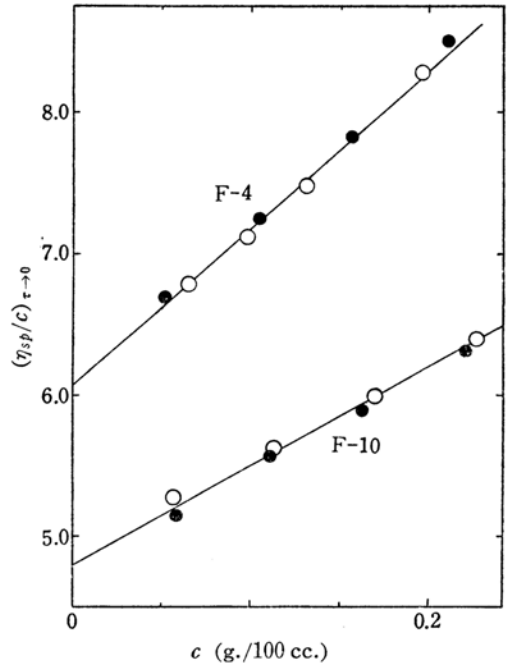

Fig. 6. $\eta_{sp}/c$ vs. $c$ relations obtained by the multi-bulb viscometer (○) and by the horizontal viscometer (●).

the conventional extrapolation such as shown in Figs. 4 and 5.

$\eta_{sp}/c$ at zero pressures, calculated from $(t/t_0)_{P\to0}$ as $((t/t_0)_{P\to1}-1)/c$ for each fraction is shown in Fig. 6 as a function of $c$. $\eta_{sp}/c$ vs. $c$ plots at zero pressure for these fractions obtained by a horizontal viscometer and reported previously[8], are inserted in the same figure for comparison's sake. The general agreement is not perfect but may be considered satisfactory taking account of the independence of the two methods employed.

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