Non-Newtonian Viscosity of Polybutadiene Solutions

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PURPOSE AND SCOPE

The need to handle flowing solutions of polymers and interest in the cause of non-Newtonian viscosity have given rise to a number of flow-stress relationships, some strictly empirical (*8, 9*) and others based on theoretical models of flow (*2, 3, 4, 6, 12, 14, 17*).

However in an attempt to correlate flow properties with molecular properties of cis-polybutadiene it was found that even for these comparatively simple and well-behaved solutions the existing treatments were inadequate. Results deviated consistently from the Ostwald-de Waele relationship with constant n and k

$$dq/dt = k\tau^n \tag{1}$$

over the stress range employed. Viscosities deviated linearly with stress from their values at zero shear, not parabolically as predicted by the theories of Eyring (*12*) and Bueche (*2, 3*). Furthermore viscosity depended on concentration in a manner inconsistent with Bueche's theory.

Closer examination showed that the flow could be described quite accurately by assuming that the viscosity decayed exponentially with stress from its value at zero shear toward a limiting value at infinite shear. Only two parameters were needed, and one of them turned out to be closely related to the polymer intrinsic viscosity. These conclusions could only be reached by taking into account the variation of stress (and viscosity) across the diameter of the tube used for measurement.

In the flow of liquids through tubes under constant pressure gradient the shear stress at a point within the tube is

$$\tau = Pr/2L \tag{2}$$

and therefore varies from 0 at the center to

$$\tau_w = PR/2L \tag{3}$$

at the wall. If the viscosity depends on shear stress, or on rate of shear, it too varies from the center of the tube to the wall, and the value calculated from the Poiseuille equation

$$\eta_a = \pi PR^4/8LQ \tag{4}$$

is apparent only and not characteristic of the wall shear stress.

In this paper the relation between true and apparent viscosity is obtained by integrating the equation of flow over the cross section of the tube, under the condition that viscosity decays exponentially with stress to a limiting value. The results are expressed graphically in a form such that the dependence of true viscosity on stress for any liquid satisfying the above condition may be obtained from apparent viscosity data by direct comparison with a master set of curves. The true viscosities can then be applied to conditions of flow other than tubular.

The present method converts apparent capillary viscosities to true viscosities without the necessity of differentiating with respect to wall shear stress (*11*). However it is applicable only to a certain class of polymer solutions, those for which viscosity decays exponentially. It remains to be seen how extensive this class is.

APPARATUS, PROCEDURE, AND MATERIALS

The viscometer was constructed principally of metal for use with nitrogen driving pressure up to 80 lb./sq. in. gauge. The measured length of the tube was 61.0 cm., but connections to it were judged to add 1.0 cm. to its effective length. The radius was determined by calibration to be 0.1337 cm., making the ratio of length to radius 456. The viscometer could be filled with enough solution for five or six flow time measurements under different driving pressures, measured by a 100 lb./sq. in. Heise gauge. The glass receiver was at atmospheric pressure and had a volume of 17.33 cc. marked off on it. The effective radius of the viscometer tube was determined and the reliability of the Heise gauge checked by calibration with glycerol and corn syrup, two Newtonian liquids whose viscosities had been determined in standard viscometers. The measurements were generally consistent to about 1%, except in a few cases when it became apparent that inhomogeneities had persisted in the most concentrated solutions.

Samples of cis-polybutadiene were prepared locally and had a cis content of about 98%. They were purified by coagulation and vacuum dried before use. The sample of polyisoprene was obtained from the Torrance, California, laboratories of Shell Chemical Company. Intrinsic viscosities were measured in toluene.* The solution of carboxymethylcellulose was obtained commercially.

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* The intrinsic viscosity of a polymer is determined from viscosity measurements in dilute solutions as the limit of $\frac{\eta/\eta_s - 1}{c}$ as $c \rightarrow o$. The conventional units for concentration of polymer solutions and intrinsic viscosity are grams per deciliter and deciliters per gram, respectively. The intrinsic viscosity is directly proportional to the equivalent hydrodynamic volume occupied by a gram of polymer in infinitely dilute solution, and is related to the molecular weight by the Mark-Houwink equation

$$[\eta] = KM^a \tag{5}$$

in which a is usually between 0.5 and 1.0.

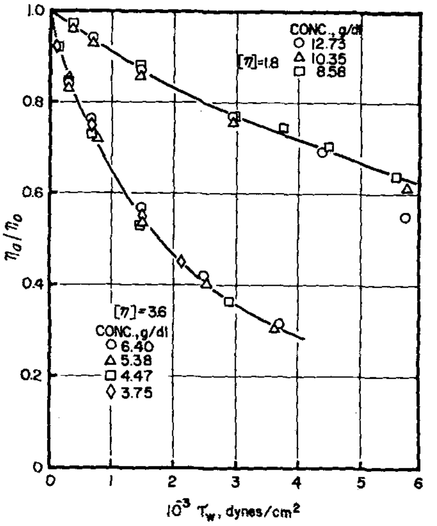

Fig. 1. Decay of apparent viscosity of benzene solutions of polybutadiene with stress, relative to viscosity at zero shear stress. Upper curve: [η] = 1.8 dl./g.; lower curve [η] = 3.6 dl./g.

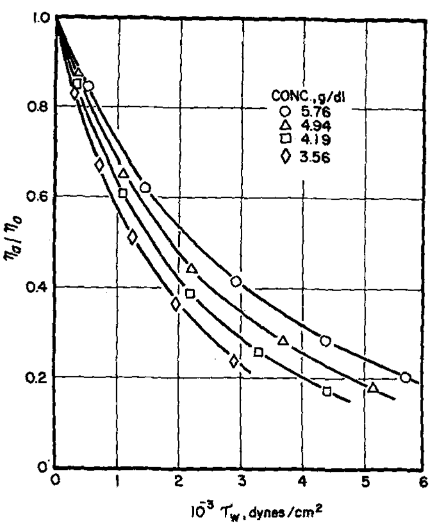

Fig. 2. Decay of apparent viscosity of benzene solutions of polybutadiene with stress, relative to zero shear stress viscosity. Effect of concentration on rate of decay. [η] = 5.25 dl./g.

Polybutadiene solutions of the highest concentration to be measured were prepared from dried samples, and solutions of lower concentration were prepared by successive dilutions of the effluents from the viscometer. All but one set of measurements were made at 25°C.

EXPERIMENTAL RESULTS

Apparent viscosities of each of the polymer solutions investigated, obtained at the five or six driving pressures, were plotted against wall shear stress, or rather driving pressure, to which it is directly proportional. The curves fitting these points resembled exponential decay curves, except that they appeared too high or too flat in the middle. On semilogarithmic paper not straight lines but downward curving arcs were obtained. It appeared likely that the true viscosity actually did decay exponentially with stress, and that deviation from exponential decay was a consequence of the variation of stress across the diameter of the tube.

In order to determine the effect of polymer concentration on the rate of decay of apparent viscosity with stress, curves for different concentrations of the same polymer sample were reduced to the same scale by dividing the apparent viscosities by the zero shear stress viscosity, obtained by extrapolation to zero stress or measurement in a standard capillary viscometer. Reduced viscosities so obtained were plotted against wall shear stress, as exemplified for three of the polybutadiene samples in Figures 1 and 2. For the cases illustrated in Figure 1 and indeed for all polymers examined having intrinsic viscosities less than 4, reduced viscosity curves for different concentrations coincide over the stress range examined. For the polybutadiene sample ($[\eta] = 5.25$) shown in Figure 2, and for the polyisoprene sample ($[\eta] = 6.3$), the curves do not coincide but instead apparent viscosity decays faster in more dilute solutions.

The main consequence of these results is that, at least for polymers of sufficiently low intrinsic viscosity, the parameters which govern the decay of viscosity with stress are independent of concentration, and knowledge of the behavior of one solution of such a polymer determines that of other solutions, given only the dependence of zero shear stress viscosity on concentration. It follows from this that the reduced viscosity of these solutions depends primarily on shear stress and not on rate of shear as implied by most formulations.

It is not at all clear why the reduced viscosity of solutions of polymers of intrinsic viscosity less than 4 should depend only on shear stress, whereas that of higher intrinsic viscosity polymers depends on both stress and concentration. Perhaps this represents transition toward primary dependence on rate of shear as described in other formulations. However analysis of the data for these cases, based on exponential decay with stress, is affected only in that one of the parameters turns out to be concentration dependent.

An exponential decay law for viscosity seems to have been first proposed by Reiner and Riwlin (*13*), but they used shear rate as the independent variable and did not attempt to integrate over the cross section of the capillary to reduce apparent viscosity to true. Other exponential or nearly exponential decay laws have appeared from time to time (*5, 7, 15*). Powell has integrated the Eyring hyperbolic function decay law for viscosity over the cross section of the capillary (*10, 16*).

CALCULATION OF FLOW CURVES

If the viscosity decays exponentially with stress to a limiting value, then

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)e^{-\sigma\tau} \tag{6}$$

or in terms of reduced viscosities $\bar{\eta} = \eta/\eta_0$ etc.:

$$\bar{\eta} = \bar{\eta}_\infty + (1 - \bar{\eta}_\infty)e^{-\sigma\tau} \tag{7}$$

The parameters $\bar{\eta}_\infty$ and σ define the stress behavior of the polymer solution.

The rate of laminar flow Q through a tube of radius R is

$$Q = \int_0^R \pi r^2(\tau/\eta)\,dr \tag{8}$$

If this is combined with Equations (2), (4), and (7) the result

$$1/\bar{\eta}_a = \int_0^R \frac{4\,r^3\,dr}{R^4\,[\bar{\eta}_\infty + (1 - \bar{\eta}_\infty)\,e^{-\sigma P r/2L}]} \tag{9}$$

is the desired relation between apparent viscosity, wall shear stress, and the parameters $\bar{\eta}_\infty$ and σ.

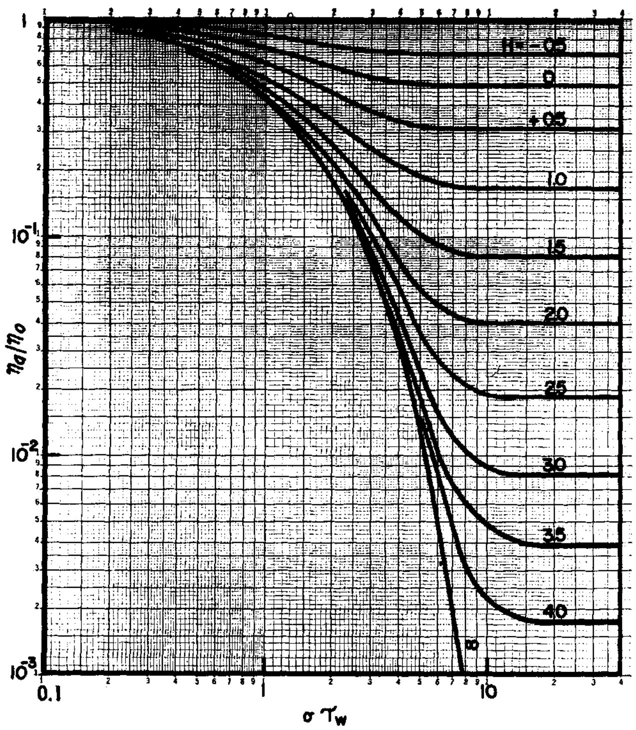

Fig. 3. Master set of curves relating apparent capillary viscosity to wall shear stress, calculated under the assumption that viscosity decays exponentially with stress.

Equation (9) is not directly integrable; however for the calculation of the curves in Figure 3 it has been integrated by three approximate methods covering overlapping but distinct regions of stress and $\bar{\eta}_\infty$ values.

The most difficult approximation, that for high shear stress, involved replacing the integrand of (9) by an appropriate cumulative probability function. To facilitate the calculation instead of $\bar{\eta}_\infty$ a related parameter H

$$H = (1/4)\ (2\pi)^{1/2} \ln (\bar{\eta}_\infty^{-1} - 1) \qquad (10)$$

was introduced. The curves of Figure 3 are given for integral and half integral values of H. H is evidently a more convenient parameter than $\bar{\eta}_\infty$ for interpolating between the curves of Figure 3.

The curve for $H = \infty$ is the limiting case for $\bar{\eta}_\infty = 0$. The viscosity of no solution obeying (6) may decay with stress faster than this.

To determine the parameters $\bar{\eta}_\infty$ and σ from apparent viscosity measurements on a given polymer solution the observed values of η_a are plotted against τ_w on the same type of logarithmic paper, superposed on the master plot of the family of curves, and, with axes kept parallel, shifted to find the curve of the master plot which most nearly fits them. This curve determines H, and from it $\bar{\eta}_\infty$ by (10); comparison of the abscissa scales gives σ, and comparison of the ordinate scales gives η_o if this is not already known from measurements at low stress.

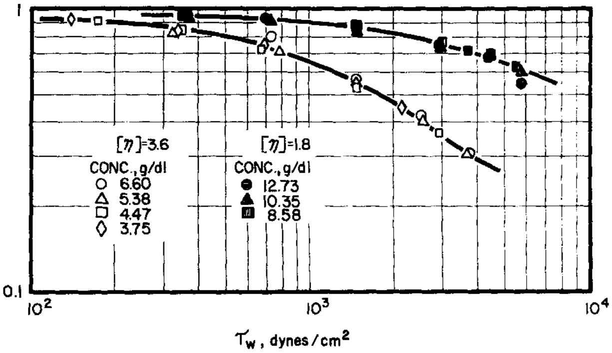

Fig. 4. Comparison of observed apparent viscosity relative to zero shear stress viscosity of polybutadiene solutions with theoretical curves. Upper curve polymer $[\eta] = 1.8$ dl./g.; lower curve $[\eta] = 3.6$ dl./g.

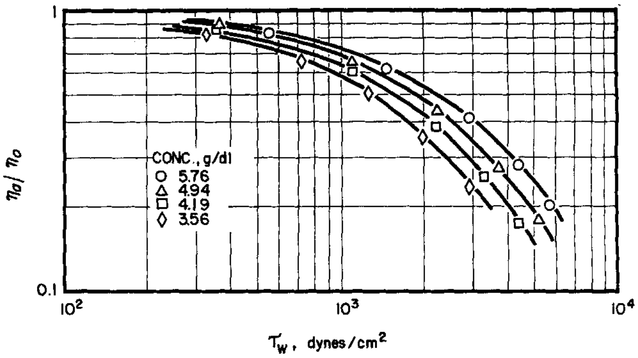

Fig. 5. Comparison of observed apparent viscosity relative to zero shear stress viscosity of polybutadiene solutions with theoretical curve. $[\eta] = 5.25$. Effect of concentration on σ.

DISCUSSION

It has been possible to fit each set of apparent viscosities to one of the curves of the master plot (or to an interpolated curve) within experimental error. For the three polymer samples selected for illustration the best fitting curves are shown in Figures 4 and 5. In these $\bar{\eta}_a$ rather than η_a has been chosen as the ordinate for convenience of presentation. The points of Figure 4 have been fitted by only one curve, analogously to those of Figure 1; in Figure 5 the set of viscosities at each concentration has been fitted separately.

The curves of Figure 3 can be converted to rate of shear vs. stress curves, and these are shown for a few values of H in Figure 6. The coordinates are such that here, as in Figure 3, only the value of H or $\bar{\eta}_\infty$ determines the curve for a given polymer solution. The line for $H = -\infty$

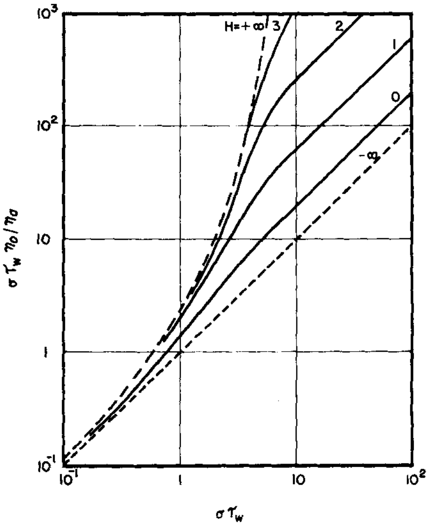

Fig. 6. Curves relating apparent wall shear rate to wall shear stress for capillary flow, with exponential decay of viscosity with stress assumed.

TABLE 1

Polymer	$[\eta]$*, dl./g.	Solvent	Conc., g./dl.	η_0, poise	H	$\bar{\eta}_\infty$	$10^4\sigma$, sq. cm./dyne
Polybutadiene	1.8	Benzene, 25°	12.73	35.0			
			10.35	11.9	0.1†	0.46	2.6
			8.58	4.7			
Polybutadiene	1.8	Benzene, 45°	12.55	15.0	0.1	0.46	2.6
			10.64	7.0	0	0.50	3.0
Polybutadiene	3.0	Benzene**	6.24	12.3	0.5	0.31	6.6
Polybutadiene	3.2	Benzene	9.73	151.0	0.5	0.31	5.9
			7.45	56.0	0.5	0.31	6.2
			6.28	20.0	0.6	0.28	5.4
Polybutadiene	3.2††	Benzene	9.01	141.0			
			7.58	54.0			
			6.79	32.0	0.5†	0.31	5.4
			5.56	11.8			
			4.51	4.5			
olybutadiene	3.6	Benzene	6.40	37.7			
			5.38	15.0	0.8†	0.22	7.2
			4.47	6.8			
			3.75	2.9			
Polybutadiene	3.6	Octane	5.73	18.5			
			4.93	8.4	0.5†	0.31	9.6
			3.81	2.24			
			3.00	0.74			
Polybutadiene	3.6	Pentene-1	8.10	70.0	1.25	0.12	3.6
			6.84	35.6	1.1	0.15	5.5
Polybutadiene	3.8	Benzene	5.64	24.4	0.9	0.19	7.6
			4.84	11.5	0.75	0.23	9.8
Polybutadiene	5.25	Benzene	5.76	122.0	1.7	0.06	4.0
			4.94	67.0	1.7	0.06	5.2
			4.19	30.5	1.7	0.06	6.0
			3.56	14.2	1.5	0.08	7.4
Polybutadiene	5.25	Octane	6.14	85.0	2.0	0.04	3.8
			4.94	35.0	2.0	0.04	5.5
			4.14	18.2	2.0	0.04	5.7
			3.64	10.6	2.0	0.04	6.4
			3.24	5.6	2.0	0.04	7.6
Polyisoprene	6.3	Hexane-isopentane	8.40	750.0	∞	0	5.8
			6.98	340.0	∞	0	8.1
			6.66	265.0	∞	0	8.6
			6.03	153.0	∞	0	10.7
			5.24	97.5	∞	0	12.0
			4.13	25.0	∞	0	18.0
Carboxymethylcellulose	—	Water	3.0	1030	∞	0	4.25
Polyisobutylene***	5.0	Decalin	9.0	4410	5.27	0.00023	5.8
			5.0	231	4.14	0.0014	15.0
			3.0	24.5	2.77	0.012	27.0
			2.0	4.65	1.97	0.042	43.0
			1.0	0.65	0.96	0.176	41.0
			0.5	0.17	0.24	0.405	42.0

* In benzene.
† From composite curve.
** This and all following at 25°C.
†† Not same sample as preceding.

*** Data taken from line graphs of reference *1*; $[\eta]$ obtained by extrapolation of η_0 to zero concentration; H calculated from observed values of η_{os}; σ obtained by curve fitting in low stress region only.

represents a Newtonian liquid, and the curve for $H = +\infty$ represents a liquid whose viscosity decays to zero. The intermediate curves have three general regions: a low stress and a high stress Newtonian region and a transition region in which (1) is approximately obeyed. Figure 6 could be employed for determining parameters instead of Figure 3 but probably with less precision because the curves lie closer together.

In Table 1 are listed the viscosity parameters and other pertinent data for the polymer solutions investigated. In accordance with this table the parameter $\bar{\eta}_\infty$ decreases as the intrinsic viscosity of the polymer increases. Measurements could not be made on solutions of polyisoprene and carboxymethylcellulose at such high stress that infinite shear stress viscosity was approached. Within the limits of experimental accuracy points for these solutions fall on the $H = \infty$, $\bar{\eta}_\infty = 0$ curve and are so recorded.

The choice of solvent does not seem to have a definite effect on $\bar{\eta}_\infty$; differences appear between benzene and octane solutions of two of the polybutadiene samples, but the differences are in opposite directions. Octane and pentene-1 are both poor solvents for polybutadiene but again appear to have opposite effects on $\bar{\eta}_\infty$ for the polymer of intrinsic viscosity 3.6. Probably these differences are within the error of curve fitting.

The parameter σ varies considerably but not with molecular weight as does $\bar{\eta}_\infty$. It becomes concentration dependent for solutions of the higher polymers and increases with dilution. If σ measures the response of molecular configuration to stress, then this response would appear to be hindered by intermolecular entanglement at the higher concentrations.

Literature data at high stress with which to test the curves of Figure 3 are rather scarce; however Brodnyan, Gaskins, and Philippoff have presented accurate flow curves for a high molecular weight polyisobutylene sample (*1*) over a wide concentration range and over the stress range of interest. Their results are replotted in Figure 7 for comparison with Figure 3.

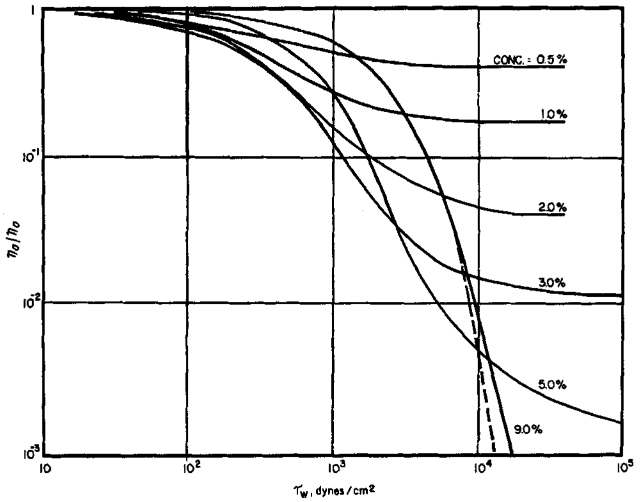

Fig. 7. Viscosity—stress plot of data of Brodnyan, Gaskins, and Philippoff for polyisobutylene in decalin. Dashed curve is part of theoretical curve $H = \infty$ fitted to the 9.0% concentration curve in the lower stress region.

Attempts to fit their results with curves of Figure 3 fail because in every case viscosity approaches its infinite stress value much more slowly than it should according to the calculated curves. In this respect their polyisobutylene differs from the author's polybutadiene, even at low values of stress.

Although the calculated curves unfortunately do not represent the behavior of polyisobutylene solution over the entire stress range, the curve $H = \infty$ does fit the lower stress portions of the flow curves for the 3.0, 5.0, and 9.0% solutions quite accurately. In fact the viscosity of the 9.0% solution conforms exactly to the curve $H = \infty$ until it has decayed to about 3% of its zero shear value. In Figure 7 the continuation of the curve for $H = \infty$ which fits the 9.0% concentration curve is shown as a dashed line. In view of this the hypothesis of exponential decay seems defensible as a starting point for description of viscosity decay. Parameters for polyisobutylene are included in Table 1, values for σ being obtained by curve fitting at low stress only.

If the value of $\bar{\eta}_\infty$ depends on the molecular weight, and σ depends on other factors such as extent of branching or chain stiffness, then a polydisperse polymer solution ought to be characterized by distributions of values of $\bar{\eta}_\infty$ and σ rather than one only. Assignment of only one value of each is a necessary approximation of curve fitting. The polyisobutylene data are explicable if the σ and $\bar{\eta}_\infty$ distributions are particularly broad and correlated so that large values of σ correspond to small values of $\bar{\eta}_\infty$.

Although the curves in Figure 3 represent flow data very well in some cases, their range of applicability is still unknown. Investigation of the effects of molecular weight distribution and branching might show if $\bar{\eta}_\infty$ and σ are dependent on them. Conversely values of the parameters, or deviation of flow curves from the calculated set, might prove to be sensitive indicators of branching or polydispersity.

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NOTATION

a, K = parameter in Mark-Houwink equation
c = concentration, g./dl.
H = parameter depending on $\bar{\eta}_\infty$
k, n = parameters in Ostwald-deWaele equation
L = length of capillary tube
M = molecular weight
P = pressure drop in capillary tube
Q = flow rate
dq/dt = rate of shear
R = radius of capillary tube
r = distance from axis of capillary tube

Greek Letters

η = absolute viscosity
η_s = solvent viscosity
η_0 = absolute viscosity at zero stress
η_∞ = absolute viscosity at infinite stress
$\bar{\eta}$ = η/η_0
$\bar{\eta}_\infty$ = η_∞/η_0
η_a = apparent (Poiseuille) capillary viscosity
$\bar{\eta}_a$ = η_a/η_0
$[\eta]$ = intrinsic viscosity
σ = decay parameter
τ = shear stress
τ_w = shear stress at wall of capillary

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