The Effect of Shear Rate on the Molecular Weight Determination of Acrylamide Polymers from Intrinsic Viscosity Measurements

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Synopsis

The rheological response of dilute solutions of high molecular weight polyacrylamides at low shear rates has been measured using a capillary viscometer that provided for a fivefold variation in shear rate at each concentration. The non-Newtonian effects were found to be significant for polyacrylamides with number-average molecular weights exceeding 10^6. The molecular weight average–intrinsic viscosity relationship most widely used in the literature, $[\eta] = 6.80 \times 10^{-4}\overline{M}_n{}^{0.66}$, was found to be valid when $[\eta]$ was measured at high shear rates where the polymer solutions approached Newtonian behavior. A new relationship was developed relating $\overline{M}_n$ to the intrinsic viscosity extrapolated to zero shear rate.

INTRODUCTION

The intrinsic viscosity measurement is a quick and easy method for molecular weight determination of high polymers that has been almost exclusively used in studying the polymerization kinetics of high molecular weight polyacrylamides. The most widely used equation relating the number-average molecular weight of these polymers with their intrinsic viscosities in water at 25°C was developed by Collinson et al.,[1]

$$[\eta] = 6.80 \times 10^{-4}\overline{M}_n{}^{0.66} \tag{1}$$

whereas the corresponding expression for the weight-average molecular weight was proposed by Scholtan[2]:

$$[\eta] = 6.31 \times 10^{-5}\overline{M}_w{}^{0.80} \tag{2}$$

Subsequent investigators of the kinetics of synthesis of acrylamide polymer from its monomer[3–8] and of the applications of these polymers in different fields such as flocculation[9] and paper making[10] as well as a recent study on the degradation of these polymers in aqueous solutions by high-speed stirring[11] have consistently used one of the previous equations to estimate the molecular weight averages for acrylamide polymers of several million molecular weight without considering the effect of shear rate on the viscosity of these solutions. However, it has been observed that even dilute solutions of high molecular weight polymers exhibit non-Newtonian behavior.[12–15] Furthermore, a pronounced effect of the shear rate on the intrinsic viscosity of a commercial nonionic acrylamide polymer (Dow Separan MGC) has been observed.[16]

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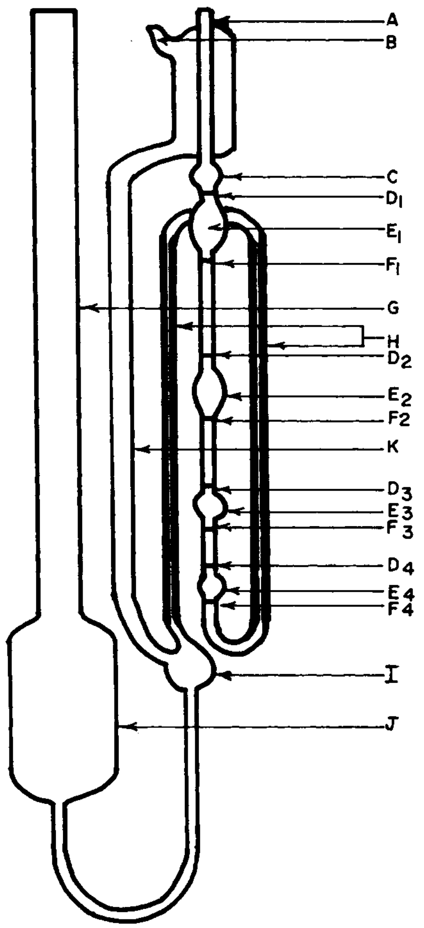

Fig. 1. The Cannon—Ubbelhode four-bulb shear dilution viscometer.

TABLE I
Flow Characteristics of the Four Bulbs of the Viscometer S 489

Bulb	t_s, sec	K
E_1	222.2	170,000
E_2	204.0	96,000
E_3	229.7	69,000
E_4	202.3	35,000

Hence, the present experimental study was undertaken to investigate the effect of shear rate on the measured intrinsic viscosity of polyacrylamides over a wide range of molecular weights and to specify standard techniques to correct for these effects so that the values obtained for the intrinsic viscosities become independent of the instrument used in their measurement.

EXPERIMENTAL DETAILS

The polyacrylamides were synthesized in aqueous solution from acrylamide monomer that had been recrystallized twice from chloroform. The water used as a polymerization medium and to dissolve the polymers for viscosity mea-

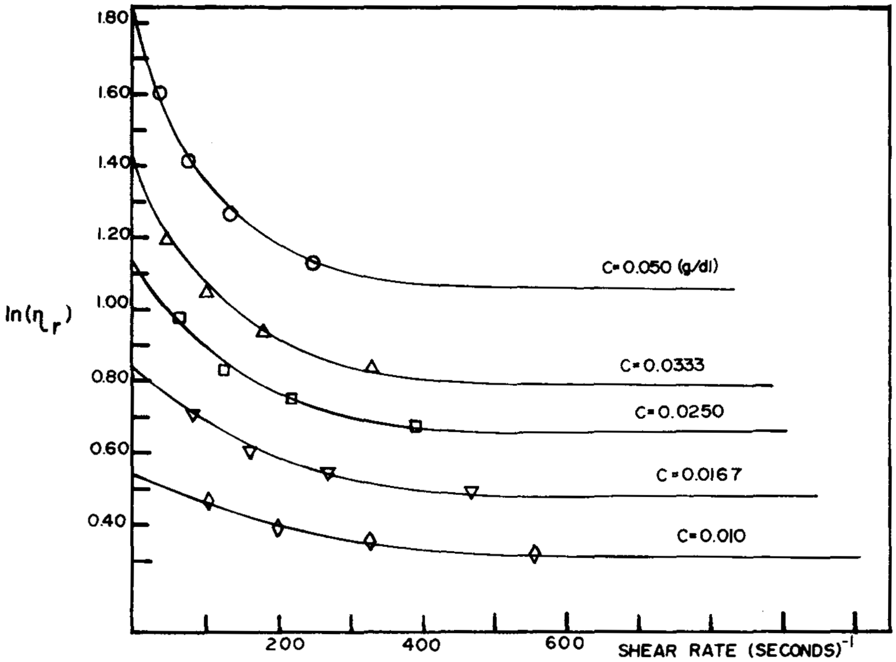

Fig. 2. Flow data for polymer (25-05-01-G).

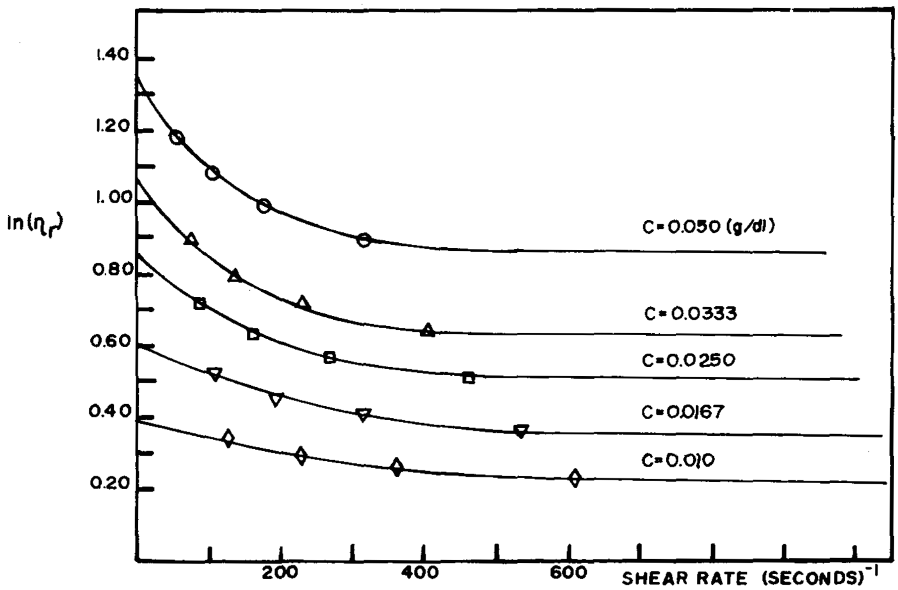

Fig. 3. Flow data for polymer (25-20-10-I).

surements was distilled twice, the second time out of an alkaline permanganate solution. The initiator used for polymerization was potassium persulfate recrystallized from twice-distilled water at 60°C. The conditions at which these polymers were synthesized will be detailed in a subsequent publication.

Figure 1 represents the Cannon–Ubbelhode four-bulb shear dilution capillary viscometer (Size 50, Serial No. S489) that was used throughout the present investigation. It was purchased from the Cannon Instrument Co., State College, Pa. The viscometer has four efflux bulbs (E_1 to E_4) providing a fivefold variation in the mean hydrostatic head between the uppermost bulb and the lowermost one. The "suspended level" device, whereby bulb I at the bottom of the capillary

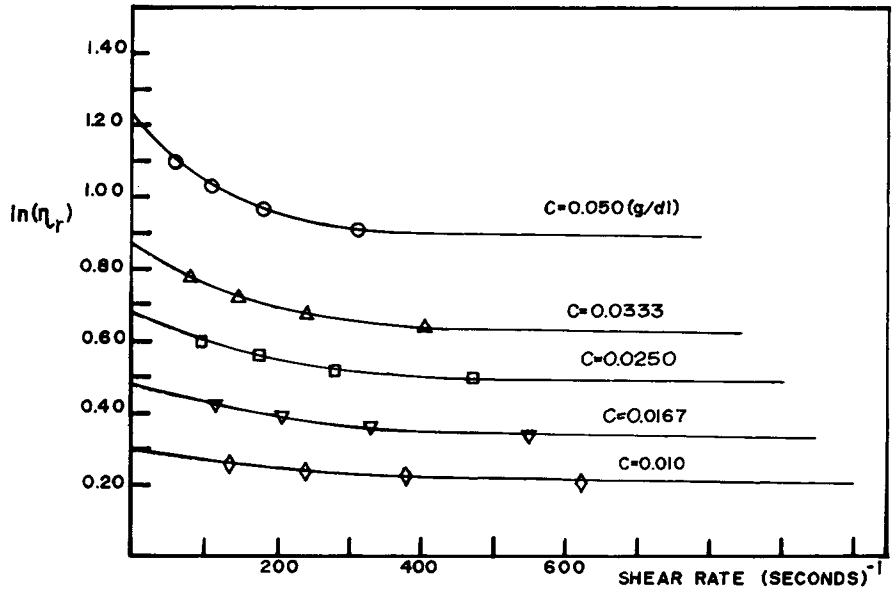

Fig. 4. Flow data for polymer (25-05-05-A).

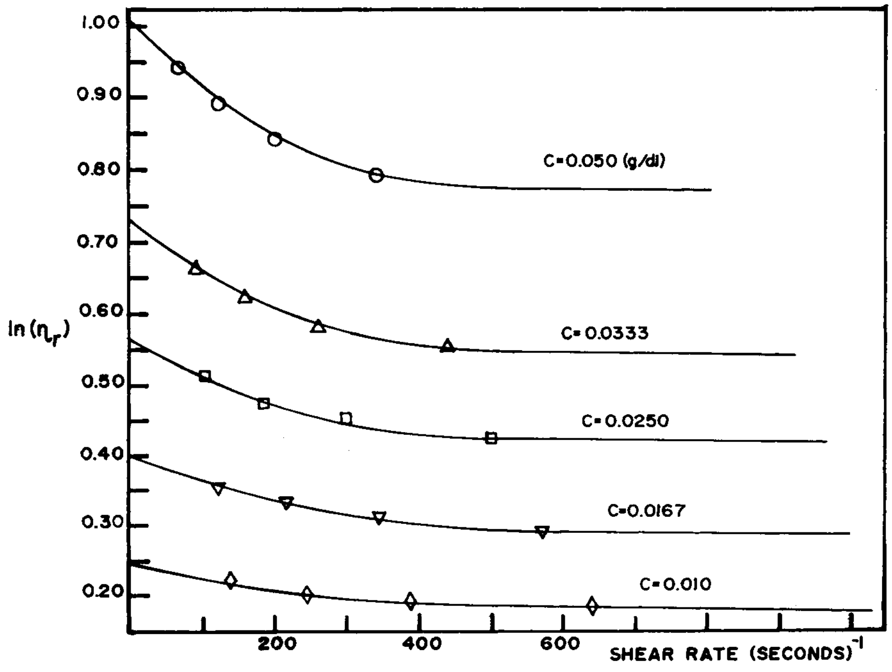

Fig. 5. Flow data for polymer (40-05-01-D).

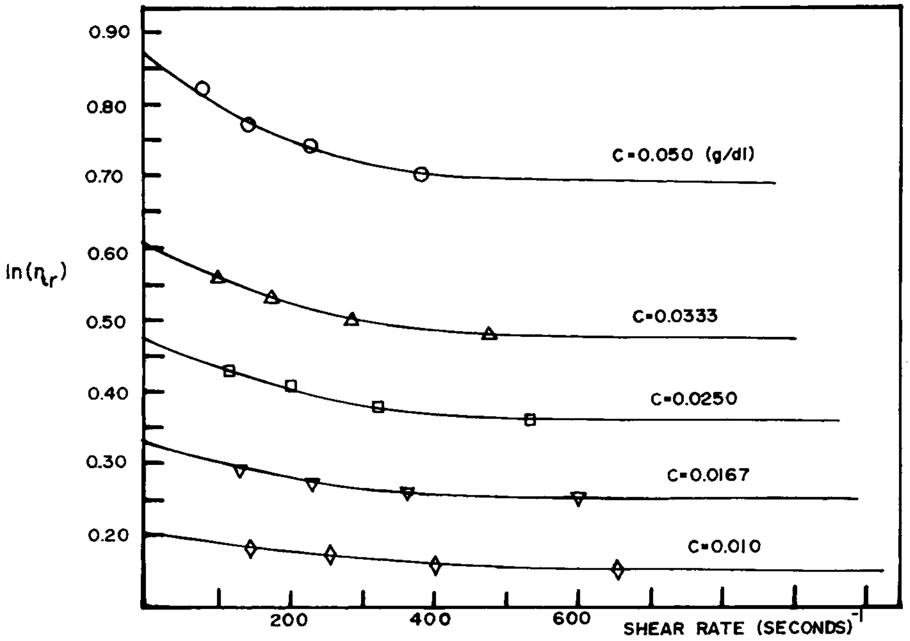

Fig. 6. Flow data for polymer (25-02-10-C).

H is connected directly to the atmosphere through tube K, makes the average hydrostatic head for each of the four bulbs independent of the amount of liquid present in reservoir J, as opposed to the standard Ostwald viscometer. All viscosity measurements were conducted in a water bath kept at 25 ± 0.1°C.

CALIBRATION OF THE VISCOMETER

It has been shown that the following equation relates the kinematic viscosity ν of a liquid to the time of flow t of a particular volume of this liquid through a capillary[17]:

$$\nu = Ct - B/t \tag{3}$$

The first term on the right-hand side of eq. (3) represents the viscous friction term, whereas the second one is a kinetic energy correction term that is significant only at low t. To evaluate B and C, two liquids whose viscosities η and densities ρ were accurately known, viz., twice-distilled water and Viscosity Standard S-3 No. 73101 supplied by the Cannon Instrument Co., were used to calibrate the viscometer. From the values of B and C thus obtained, it was established that even for pure water, where t is minimum in the present case, the kinetic energy term B/t is less than 2% of the viscous term Ct for each of the four bulbs and hence may be neglected. Furthermore, neglecting the change in density of the polymer solutions over the range of concentrations involved in measuring $[\eta]$, eq. (3) reduces to

$$\eta = C't \tag{4}$$

Therefore, the relative viscosity η_r, defined as the ratio of solution viscosity η to the viscosity of the solvent η_s, can be expressed as

$$\eta_r \equiv \eta/\eta_s = t/t_s \tag{5}$$

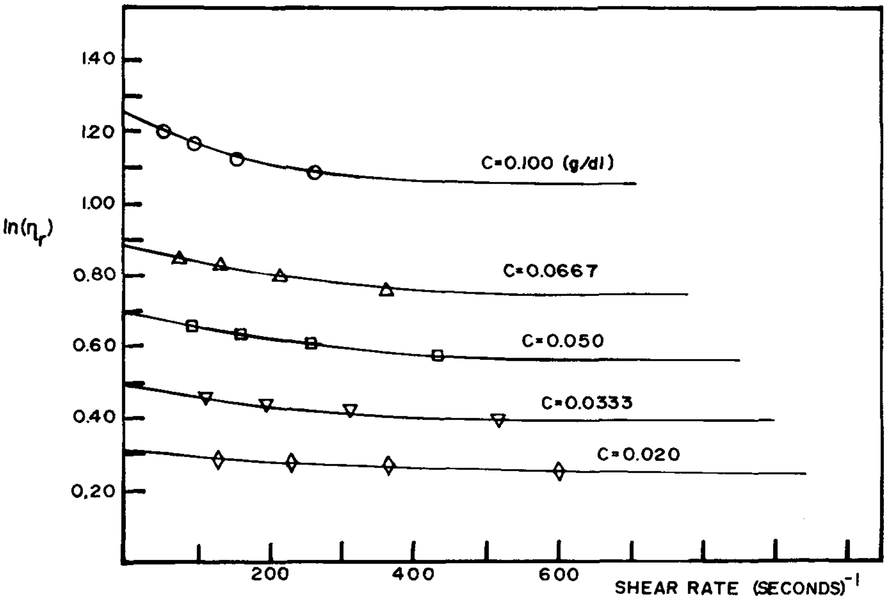

Fig. 7. Flow data for polymer (40-05-05-A).

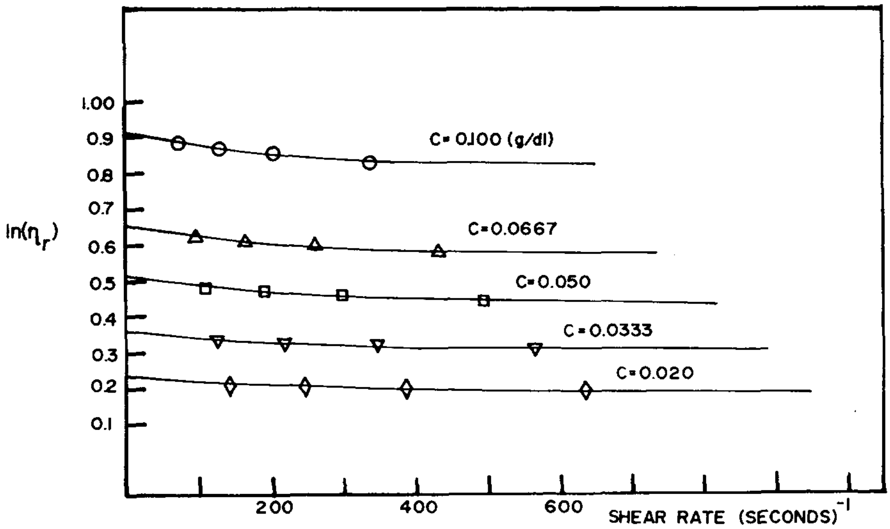

Fig. 8. Flow data for polymer (40-02-05-A).

where t is the time of flow of a certain volume of solution through the capillary and t_s is the time of flow of an equal volume of solvent under the same conditions. Equation (5) was used to calculate the relative viscosity η_r and the specific viscosity η_{sp} defined by

$$\eta_{sp} \equiv \eta_r - 1 = (\eta - \eta_s)/\eta_s \tag{6}$$

The intrinsic viscosity $[\eta]$ was then calculated from its definition

$$[\eta] \equiv \left(\frac{\ln \eta_r}{C}\right)_{C\to 0} = \left(\frac{\eta_{sp}}{C}\right)_{C\to 0} \tag{7}$$

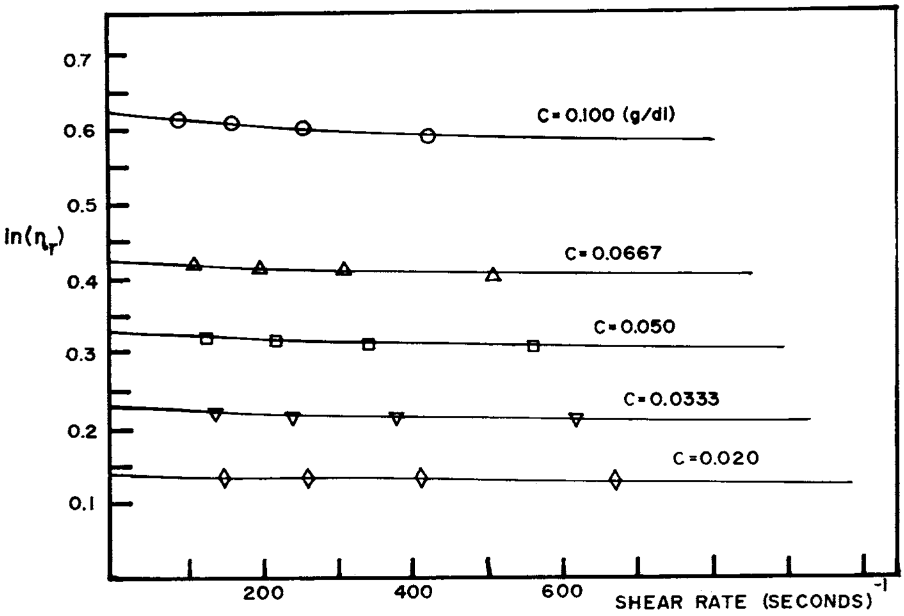

Fig. 9. Flow data for polymer (40-05-25-B).

The shear rate at the wall of the capillary, $\dot{\gamma}_w$, was calculated from the following expression[14]:

$$\dot{\gamma}_w = RHg\rho/2L\eta \tag{8}$$

where R and L are the radius and length of the capillary, respectively; H is the average distance between the upper and lower liquid levels; g is the acceleration of gravity, ρ is the liquid density; and η is the liquid viscosity. From eqs. (4) and (8) it is clear that $\dot{\gamma}_w$ may be computed from the time of flow t as follows:

$$\dot{\gamma}_w = \left(\frac{RHg\rho}{2LC'}\right)\frac{1}{t} = \frac{K}{t} \tag{9}$$

where K is a constant for each bulb, usually referred to as the "shear rate constant." Table I lists the time of flow of twice-distilled water, t_s, through each of the bulbs (averaged over ten readings) and the corresponding values of the shear rate constant K calculated from the specifications of the viscometer that were provided by the manufacturer.

RESULTS AND DISCUSSION

Figures 2 to 9 represent some typical viscosity data of some of the polymers tested that span the molecular weight range investigated. From these figures it is clear that these solutions exhibit significant non-Newtonian behavior even at the low concentrations encountered in the estimation of the intrinsic viscosities. The rate of change of the viscosity with shear rate increases with increasing concentration and with increasing molecular weight. It also decreases with increasing shear rate, the solutions approaching Newtonian behavior at high shear rates. The last observation suggests that two of the methods found in the lit-

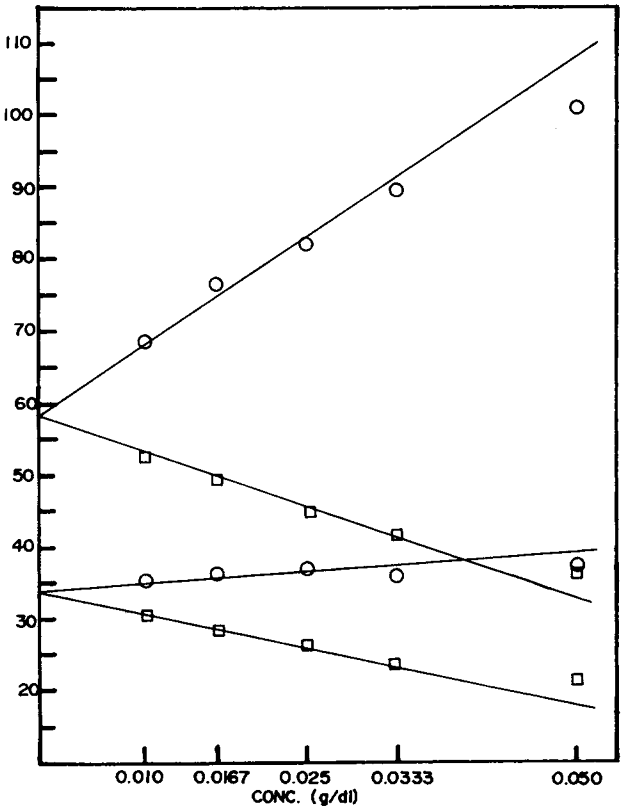

Fig. 10. Intrinsic viscosities for polymer (25-05-01-G): (□) (ln η_r)/C, (g/dl)$^{-1}$; (○) η_{sp}/C, (g/dl)$^{-1}$.

TABLE II
Intrinsic Viscosities of Standards A and B

	Standard A	Standard B
$[\eta]^{20}$	11.41	8.17
$[\eta]_\infty$	12.30	8.40
$[\eta]_0$	17.70	10.40

erature to correct for the effect of shear rate are valid for the polyacrylamide–water system, viz., either to extrapolate the data to zero shear rate[13,14] or to extrapolate to high enough shear rates where the non-Newtonian behavior is minimal.[12] Attempts to linearize the flow data according to the methods previously suggested[18,19] were unsuccessful. Therefore, the viscosity data were extrapolated "by eye" to both high and zero shear rates, as shown in Figures 2 to 9. The values for ln η_r at both these limits were obtained for each concentration. Then plots of (ln η_r)/C and η_{sp}/C versus the concentration C (in g/dl) were prepared, then they were extrapolated to zero concentration to obtain values for the intrinsic viscosities at zero shear rate, $[\eta]_0$, and at high shear rate, $[\eta]_\infty$. This procedure is illustrated in Figures 10 to 17 for the polymers whose flow data were shown in Figures 2 to 9.

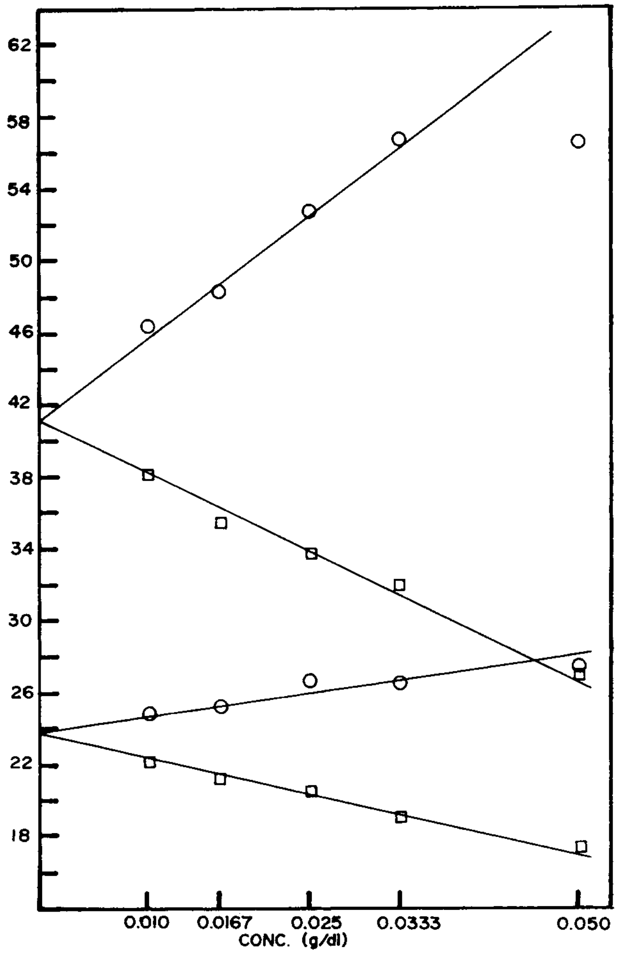

Fig. 11. Intrinsic viscosities for polymer (25-20-10-I): (□) (ln η_r)/C, (g/dl)$^{-1}$; (○) η_{sp}/C, (g/dl)$^{-1}$.

Figures 10 to 17 clearly show that the effect of the rate of shear on the intrinsic viscosities becomes more pronounced for the higher molecular weight polymers. Figure 18 illustrates this fact clearly, where $[\eta]_0$ is plotted versus $[\eta]_\infty$ for all the polymers tested, together with a line of 45° slope representing Newtonian behavior.

Figures 2 and 10 represent the behavior of polyacrylamide (25-05-01-G) that has one of the highest molecular weight averages encountered in the present investigation. By using a traditional single-bulb viscometer to estimate $[\eta]$, the magnitude of the resulting $[\eta]$ would strongly depend on the shear flow characteristics of the instrument used. The magnitude of the possible variation in the value of $[\eta]$ may be as high as that of the ratio $[\eta]_0/[\eta]_\infty$, which is equal to 1.73 for this particular polymer. The corresponding variation in the molecular weight averages calculated from eqs. (1) and (2) are 2.30 and 1.98, respectively.

On the other hand, Figures 9 and 17 represent the viscosity data for one of the smallest molecular weight polyacrylamides encountered. It is clear that its so-

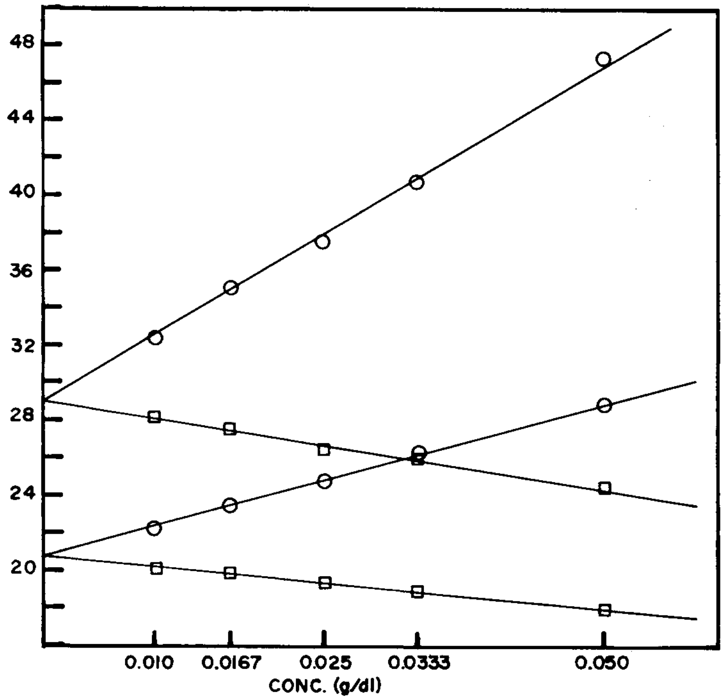

Fig. 12. Intrinsic viscosities for polymer. (25-05-05-A): (□) (ln η_r)/C, (g/dl)$^{-1}$; (○) η_{sp}/C, (g/dl)$^{-1}$.

lutions conformed closely to Newtonian behavior. From eq. (1), $\overline{M}_n$ for this polymer is in the order of one million. Therefore, this may be regarded as a critical molecular weight above which the non-Newtonian aspects of the polyacrylamide solutions may not be ignored.

It may be noted that ordinary extrapolation to infinite dilution applied to measurements made with a single-bulb viscometer will fail to correct for the error ensuing from non-Newtonian behavior. This is clear from Figures 2 to 9, which show that the shear rate at which any one of the bulbs operate increases with each subsequent dilution for each polymer solution. Moreover, for solutions having the same concentration of polymers with different molecular weights, the viscometer will operate at a different shear rate for each polymer due to the difference in viscosity.

The above results agree qualitatively with those observed for dilute solutions of polyisobutylene[13] and polystyrene.[14] However, for these polymers the logarithm of their specific viscosity was found to decrease linearly with increasing shear rate except for the highest molecular weight fractions. On the other hand, the present results indicate that this relationship is always nonlinear for aqueous polyacrylamide solutions. This was also observed for dilute Alfin polyisoprene solutions in benzene.[19]

It may be noted that Figures 2 to 9 indicate that the apparent viscosities of the polyacrylamide solutions show no sign of leveling off to limiting Newtonian values at low shear rates. However, flow data for polyacrylamide gathered through a Weissenberg rheogoniometer[16] indicated that the solutions did not

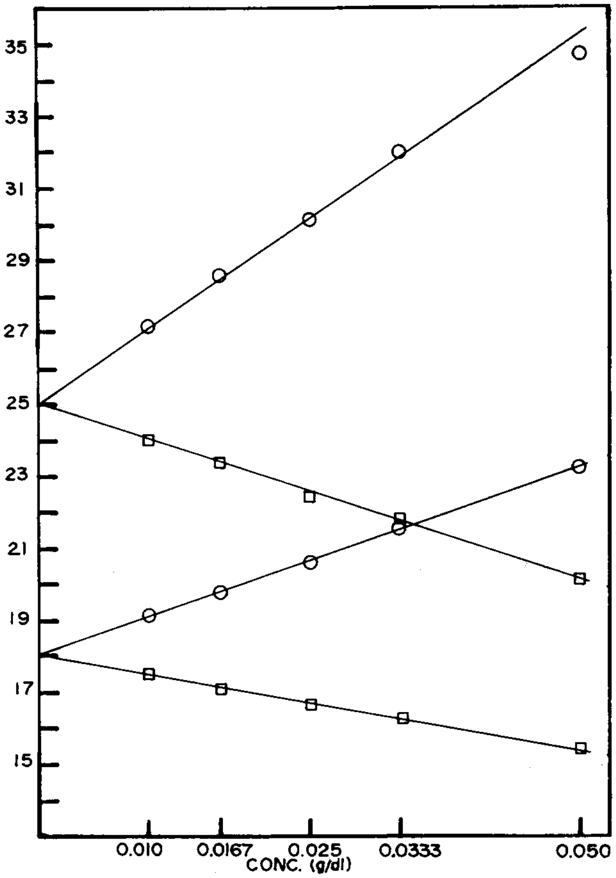

Fig. 13. Intrinsic viscosities for polymer (40-05-01-D): (□) (ln η_r)/C, (g/dl)$^{-1}$; (○) η_{sp}/C, (g/dl)$^{-1}$.

reach their limiting low-shear values until the shear rates were in the order of 1 to 10 sec^{-1}. Such low shear rates are difficult to achieve in capillary viscometers. This also accounts for the fact that previous investigators that have used capillary viscometers to investigate other polymer systems failed to detect such a low-shear limiting viscosity.[13,14,19] However, capillary viscometers are still favored for intrinsic viscosity determination because they allow dilutions to be performed *in situ,* thereby greatly reducing measurement times.

INTRINSIC VISCOSITY–MOLECULAR WEIGHT RELATIONSHIPS

For an unfractionated polymer with a wide molecular weight distribution, an intrinsic viscosity measurement will yield an estimate of the viscosity-average molecular weight $\overline{M}_v$. However, the estimation of the kinetic parameters in the free-radical polymerization model requires the knowledge of the number-average molecular weight $\overline{M}_n$. Although in principle $\overline{M}_n$ may be estimated by gel permeation chromatography (GPC), a previous attempt to do so for high molecular

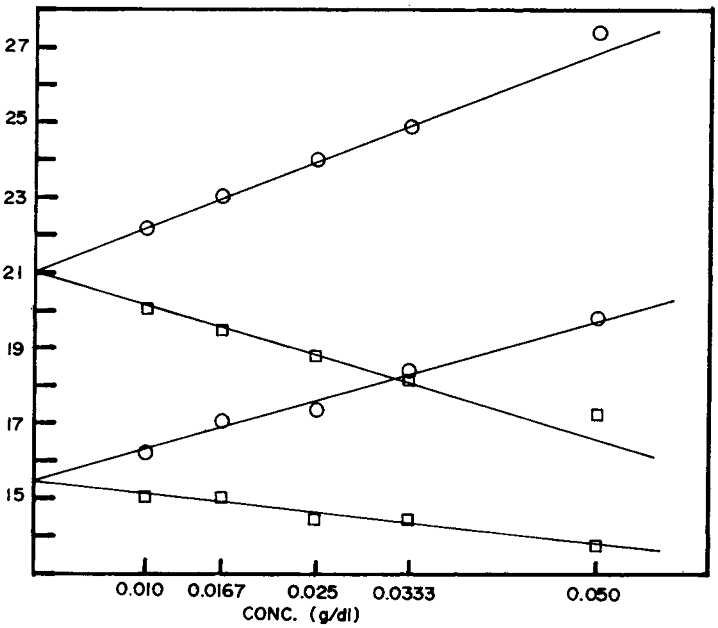

Fig. 14. Intrinsic viscosities for polymer (25-02-10-C): (□) (ln η_r)/C, (g/dl)$^{-1}$; (○) η_{sp}/C, (g/dl)$^{-1}$.

weight polyacrylamides was not satisfactory due to the limited resolution by the packing material of the high molecular weight tail of those polymers.[8] Present attempts to estimate the molecular weight distributions of the synthesized polyacrylamides by GPC were also unsuccessful for the same reason, despite the use of the packing material recently developed by E. Merck, Darmstadt, Germany, with a mean pore diameter as high as 1400 nm. The columns were calibrated by the polyacrylamide standards A and B synthesized by Abdel-Alim and Hamielec.[20] When the calibration line thus obtained was used to estimate the molecular weight distribution of a polyacrylamide with a higher molecular weight than these standards, such as polymer (25-05-01-G), the polydispersity was found to be significantly less than 2.0, which is impossible according to the free-radical polymerization theory. This, together with the fact that the leading portions of the chromatograms for polymers with average molecular weights estimated from eq. (1) ranging from 3.0×10^6 to 10.0×10^6 all started nearly at a constant retention volume, indicated that the hydrodynamic volumes of these polymers exceeded the exclusion limit of the GPC columns.

Two methods have been proposed in the literature to obtain $\overline{M}_n$ from intrinsic viscosity measurements. Both make use of the fact that, in acrylamide polymerization, termination is mainly through disproportionation and that, when the molecular weight average of the resulting polymers is as high as a few million, the transfer to monomer reaction is dominant in controlling the molecular weight.[8] It follows that the polyacrylamides obtained under isothermal conditions in free-radical polymerization and in the absence of substantial amounts of a chain transfer agent will have a molecular weight distribution very close to the "most probable distribution."[21]

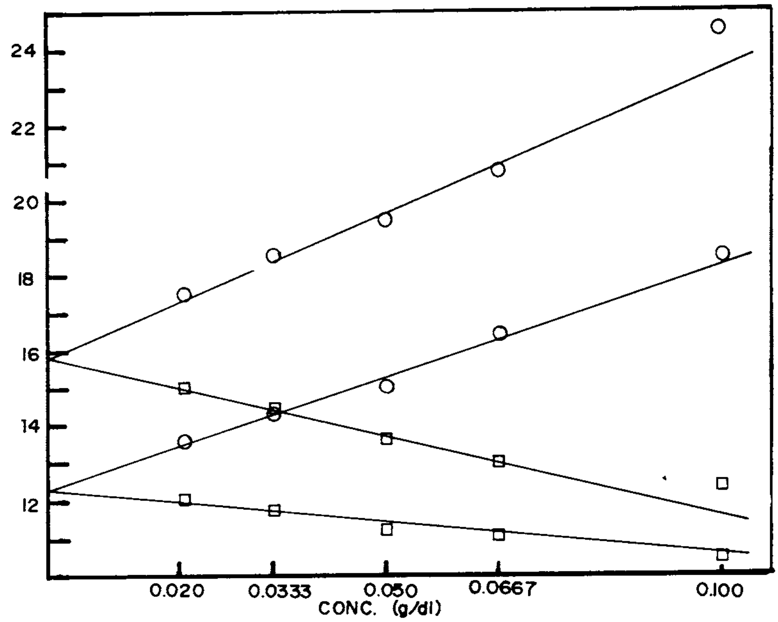

Fig. 15. Intrinsic viscosities for polymer (40-05-05-A): (□) (ln η_r)/C, (g/dl)$^{-1}$; (○) η_{sp}/C, (g/dl)$^{-1}$.

Proponents of the first method for obtaining $\overline{M}_n$ from [η] argue that the viscosity-average molecular weight will always be considerably closer to the weight-average than the number-average molecular weight for any distribution likely to be encountered in a high polymer.[4,5,22] Therefore, eq. (2) is used to obtain $\overline{M}_w$ from the measured [η]. And, as the polydispersity of the most probable distribution is 2.0, $\overline{M}_w$ is divided by 2.0 to obtain $\overline{M}_n$. Inspection of eq. (2), with $(\overline{M}_w)^{0.80}$ replaced by $(2\,\overline{M}_n)^{0.80}$, reveals that the net effect of this method is to use the following expression to calculate the number-average molecular weight:

$$[\eta] = 1.10 \times 10^{-4}\overline{M}_n{}^{0.80} \qquad (10)$$

Other investigators have argued that a molecular weight exponent of 0.80 in eq. (2) is high in view of the fact that water is not considered to be a "good" solvent for polyacrylamide.[1] Furthermore, Ishige and Hamielec[8] have shown that eq. (1) predicted values for $\overline{M}_n$ in close agreement with those obtained by electron microscopy and light scattering for polyacrylamides with the most probable distribution. Hence, several investigators chose to use eq. (1) directly to estimate $\overline{M}_n$ for polyacrylamides with such a molecular weight distribution.[3,6,8,23]

It is this latter approach that was adopted in the present investigation. However, the shear conditions under which eq. (1) was shown to be valid for high molecular weight polyacrylamides with the most probable distribution remained to be determined. In the original investigations,[8,20] the intrinsic viscosities of these polymers were measured using a traditional single-bulb capillary viscometer, with no shear rate correction. Table II summarizes the values of [η] thus obtained, together with the values of [η]$_0$ and [η]$_\infty$ presently obtained by the

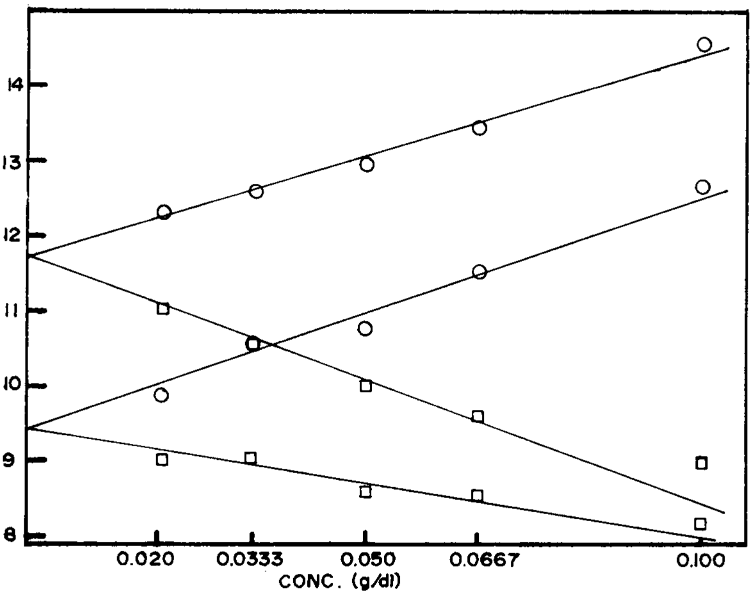

Fig. 16. Intrinsic viscosities for polymer (40-02-05-A): (□) (ln η_r)/C, (g/dl)$^{-1}$; (○) η_{sp}/C, (g/dl)$^{-1}$.

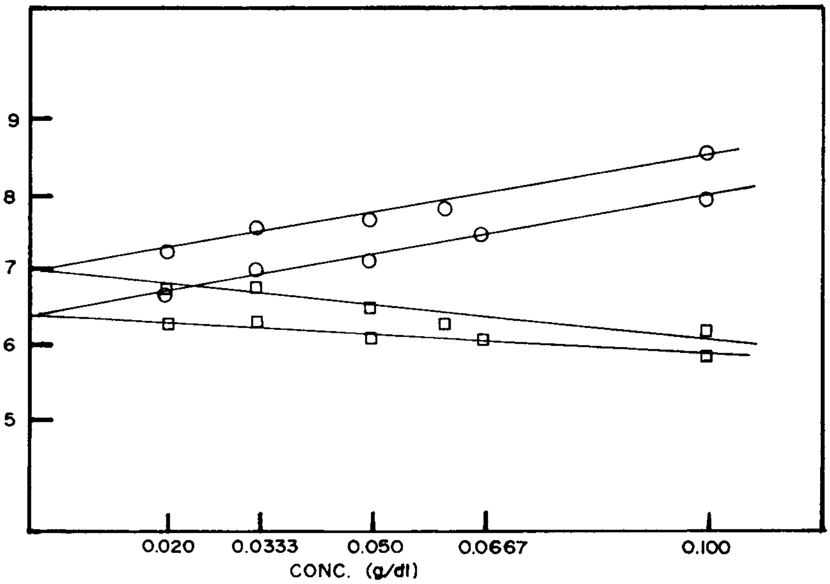

Fig. 17. Intrinsic viscosities for polymer (40-05-25-B): (□) (ln η_r)/C, (g/dl)$^{-1}$; (○) η_{sp}/C, (g/dl)$^{-1}$.

four-bulb viscometer. It is clear that the values of $[\eta]$ originally reported closely approximated those of $[\eta]_\infty$. Indeed, from the specifications of the two viscometers used by the original investigators to obtain $[\eta]$,[24] it was possible to determine that the shear rate conditions prevailing in these viscometers were

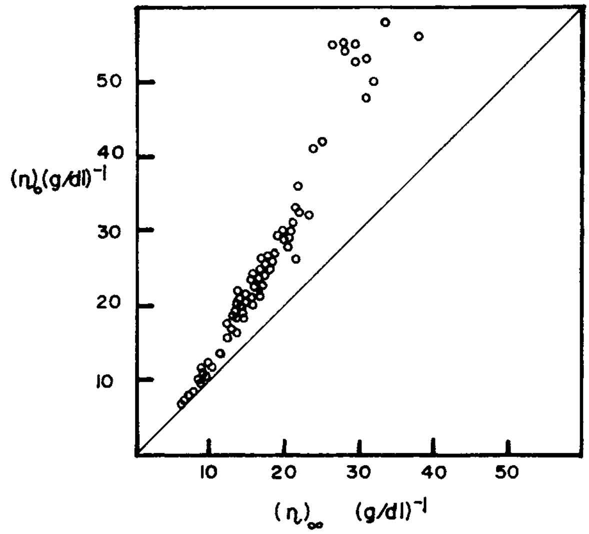

Fig. 18. Intrinsic viscosities at zero shear rate vs intrinsic viscosities at high shear rates.

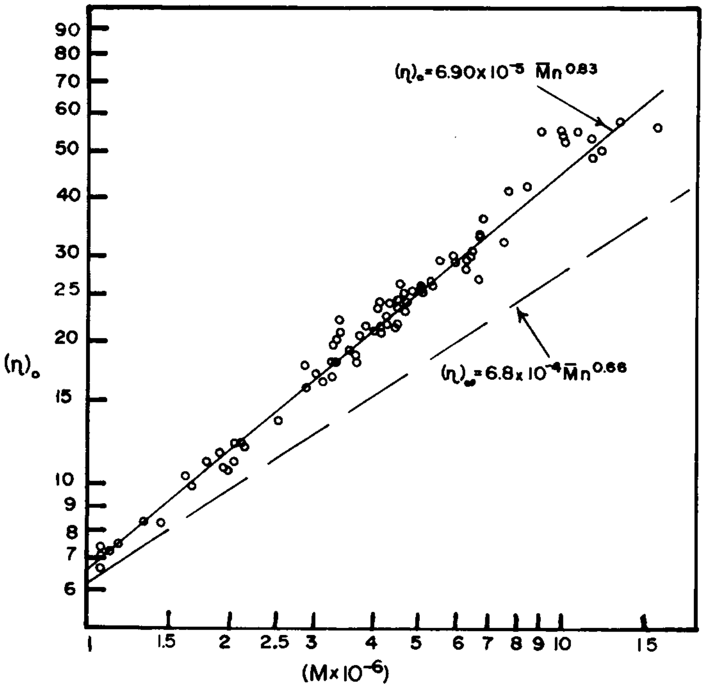

Fig. 19. Relationship between molecular weight and intrinsic viscosity at zero shear rate.

almost identical to those associated with the uppermost bulb of the four bulb viscometer presently used. From Figures 2 to 9 it is clear that a viscometer with such shear characteristics will fortuitously approximate the values of $[\eta]_\infty$. In other words, eq. (1) has been proved valid for high molecular weight polyacrylamides having the most probable distribution when $[\eta]$ is measured at high shear rates.

Therefore, the molecular weight averages of all the polymers examined in the present investigation were thus calculated. These values for $\overline{M}_n$ were then plotted against $[\eta]_0$ on a logarithmic plot, as shown in Figure 19. The solid line in this figure may be expressed as

$$[\eta] = 6.90 \times 10^{-5}\overline{M}_n{}^{0.83} \tag{11}$$

Therefore, eq. (11) should be used to estimate $\overline{M}_n$ when the viscosity data are extrapolated to zero shear rate to obtain $[\eta]_0$, whereas eq. (1) should be used in conjunction with $[\eta]_\infty$.

CONCLUSIONS

The non-Newtonian aspects of the rheological response of dilute solutions of polyacrylamides having a number-average molecular weight in excess of 10^6 (or an intrinsic viscosity larger than about 6.0 to 7.0) were found to be significant. It was shown that for the highest molecular weight polymers, neglecting to correct for shear rate effects in measuring the intrinsic viscosity may introduce an error in excess of 100% of the value of the computed average molecular weight.

Equation (1) was found to be valid when the intrinsic viscosity is measured at high shear rates where the polymer solutions approach Newtonian behavior. A new relationship, eq. (11), was developed to be used in conjunction with the intrinsic viscosity estimated at zero shear rate, $[\eta]_0$.

A value approximating $[\eta]_\infty$ may be obtained from measurements done in a single-bulb viscometer provided that it operates at high enough shear rates. However, an upper limit on the rate of shear is imposed by the requirement that the kinetic energy correction term in eq. (3) be negligible in comparison with the viscous term so that eq. (5) may be used to estimate the relative viscosity. On the other hand, $[\eta]_0$ of a polyacrylamide with $\overline{M}_n$ much in excess of 10^6 cannot be approximated closely with a single-bulb viscometer because of the excessive curvature of the flow curves at low shear rates.

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