

On the Characterization of Non-Newtonian Flow. II

RAFFAELE SABIA, *W. R. Grace & Company, Polymer Chemicals
Division, Clifton, New Jersey*

Synopsis

A new rheological method for the determination of the molecular weight distribution of polymers was developed using the critical viscosity for entanglement together with the Newtonian viscosity and the apparent viscosity at a shear stress in the non-Newtonian region. Alternately, two shear stresses in the non-Newtonian region may be used. It was established that the critical molecular weight for entanglement is independent of the shear stress but dependent on the shear rate.

INTRODUCTION

A rheological method for the determination of a molecular weight distribution factor was proposed in a previous paper.¹ Based on the work of F. Bueche² and Bueche and Harding,³ it involved the determination of a master curve for the non-Newtonian behavior of a given polymer and a curve-fitting procedure. In this paper, a new and different approach is proposed. It does not require either of the above steps. The two methods complement each other since the former yields information as to molecular weight while the latter requires some information not readily available.

The familiar logarithmic viscosity-molecular weight plot for polymer melts yields a relationship made up of two linear portions. The one at low viscosities has a slope in the range of 1-2 and averaging 1.6; at high viscosities the slope of the line is 3.4.⁴ F. Bueche⁵ has interpreted the change in slope as the onset of entanglements and was able to predict a slope of 3.5. The point of intersection, \bar{M}_c is the critical molecular weight for entanglement.

Bagley and West⁶ have shown recently that for molecular weights above \bar{M}_c analogous plots of the apparent non-Newtonian viscosities versus molecular weight yield a series of straight lines intersecting at a point corresponding to \bar{M}_c . The slopes of these lines decrease with increasing shear rate (Fig. 1). Porter and Johnson^{7,8} have extended this analysis to other systems. The conclusions drawn⁶ are: "First, non-Newtonian flow behavior . . . occurs only when the chains are long enough to entangle. Second, the critical molecular weight for entanglement to occur is independent of shear rate. Finally, . . . the effectiveness of the entanglements must be decreasing with increasing shear rate." It is interesting to note that both

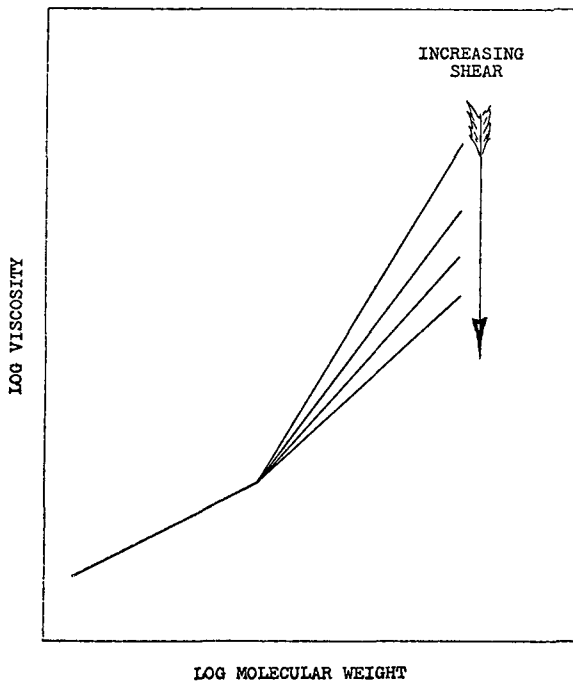


Fig. 1. Relationship between viscosity and molecular weight as a function of shear.

data at constant shear rate⁶ and at constant shear stress⁷ yielded reasonable values for \bar{M}_c .

MATHEMATICAL RELATIONS

On taking the point of inflection in Figure 1 as the origin, one can easily derive

$$\log \eta_0 - \log \eta_c = m (\log \eta - \log \eta_c) \quad (1)$$

or

$$\log \eta/\eta_0 = [(m - 1)/m] \log \eta_c/\eta_0 \quad (1a)$$

for molecular weight above \bar{M}_c at constant shear. η_0 and η are the Newtonian and non-Newtonian viscosities, respectively; η_c is the critical viscosity for entanglement. The slope, m , is given by $3.4/\alpha$, where α is the slope in Figure 1 with increasing shear. If the lower limit of α is taken to be one, the maximum value of m is 3.4. Permitting higher values of m , eq. (1a) predicts a second Newtonian region at very high shear independent of molecular weight. A second Newtonian region has been observed for polymer solutions. Onogi, Hamana, and Hirai⁹ report that the effect of molecular weight is insignificant at high frequencies for a 15% solution of polyvinyl alcohol.

The problem can now be stated very simply. Our previous work¹ has indicated that for two polymers having the same zero shear viscosity, the one having the broader molecular weight distribution exhibits non-Newtonian flow at a lower shear. This is substantiated by similar observations in the literature.^{10,11} Stated differently, the slope m is a function of the molecular weight distribution.

EXPERIMENTAL

A number of high density polyethylenes have been characterized as to their Newtonian viscosities and molecular weight distribution by the method previously described¹ by using shear stress-shear rate data obtained with a gas-operated extrusion rheometer and a capillary having a length/diameter ratio of 19.4. No corrections were applied.

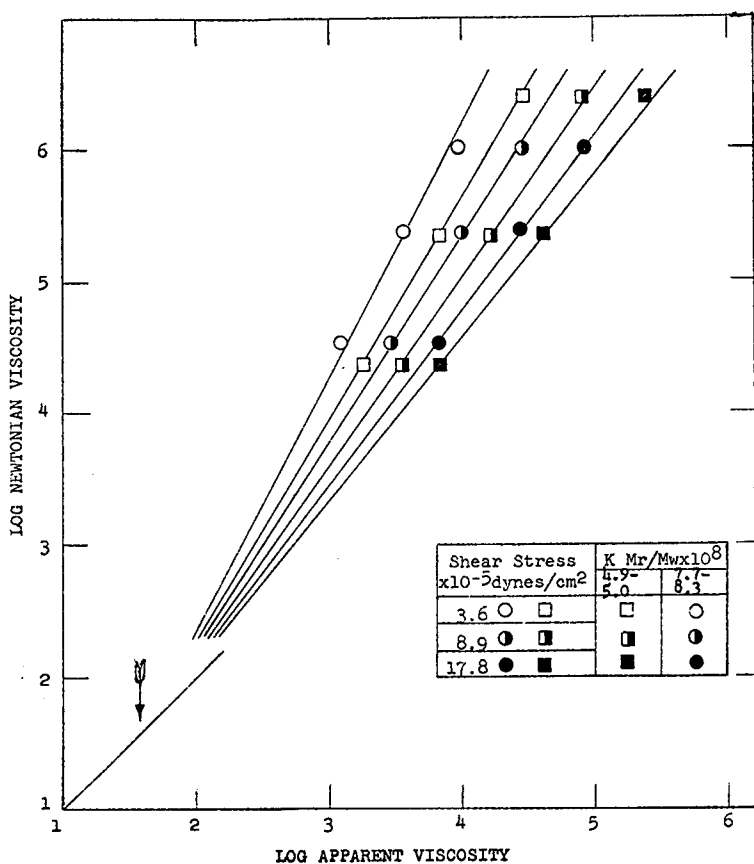


Fig. 2. Viscosity relationships at constant shear stress for polyethylene of varying molecular weight distribution ($K M_r/M_w \times 10^8$).¹

RESULTS

Two series of resins, differing in their rheological distribution factor¹ ($K \bar{M}_w / \bar{M}_v \times 10^8$), were chosen for analysis. The Newtonian viscosities are plotted, in Figures 2 and 3, against the apparent viscosities at constant shear stress and shear rate, respectively, according to eq. (1). The shear rates and shear stresses used were chosen within the range experimentally available to our instrument. The point of intersection, η_c , must come on

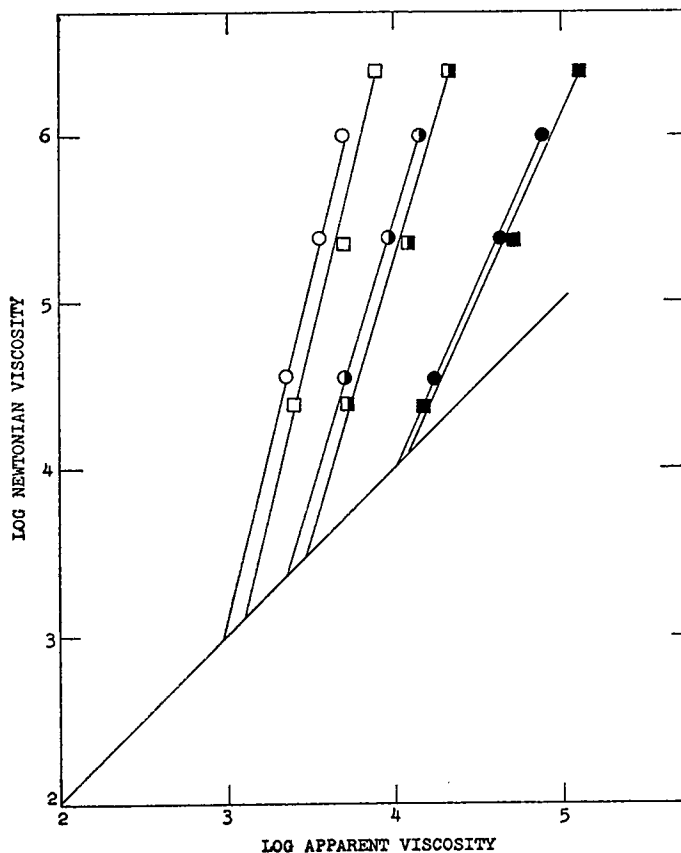


Fig. 3. Viscosity relationships at constant shear rate: (O, □) 5 sec.⁻¹; (◐, ◑) 100 sec.⁻¹; (●, ■) 500 sec.⁻¹

the line of unit slope if the critical molecular weight for entanglement is independent of shear. This is observed for data at constant shear stress but not at constant shear rate. If, rather than the Newtonian viscosity, one had used an apparent viscosity at some high shear for the ordinate, intercepts on the line of unit slope could have been obtained in both cases, but their values would have differed and the whole procedure cast in doubt. One would also have been misled if these resins had not been characterized,

a priori, as to their molecular weight distribution. As is, the drift observed with the circles was traced to too broad a distribution range in that series.

Polystyrene

Having established that the critical molecular weight for entanglement is independent of shear stress, the functionality between m and the molecular weight distribution may be experimentally examined. Rudd¹⁰ has characterized a series of polystyrenes by the zero-shear viscosity (by extrapolation), the viscosity at 10^7 dynes/cm.² and the molecular weight distribution

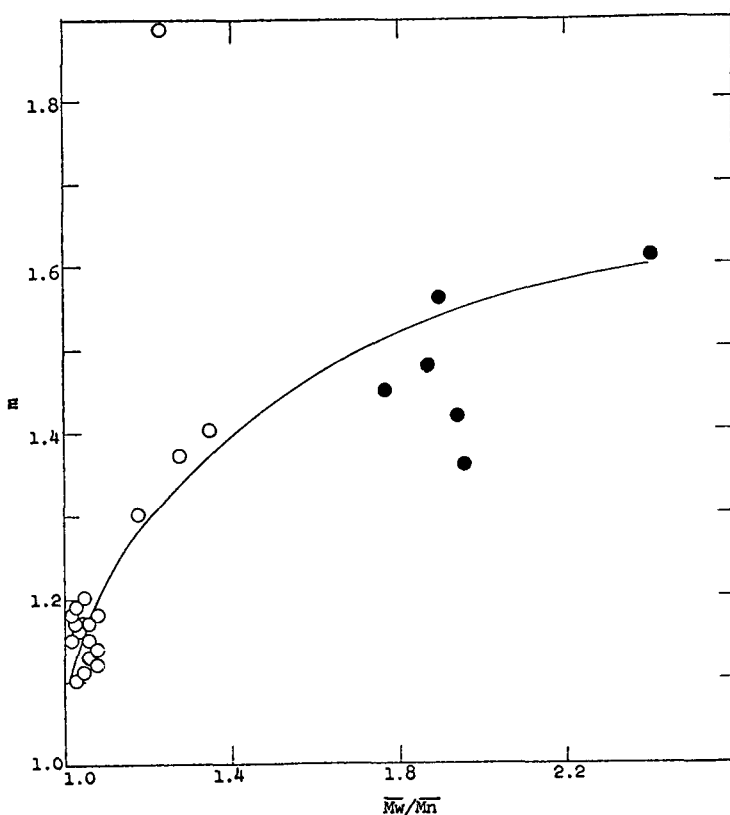


Fig. 4. Molecular weight distribution relationships for (O) anionic and (●) isothermal polymerized styrene.

(\bar{M}_w/\bar{M}_n) . Values for m have been calculated from these data and plotted against \bar{M}_w/\bar{M}_n in Figure 4. For the $\log \eta_c$ at 227°C . a value of 1.6 was used which, according to Rudd, corresponds to a weight-average molecular weight of 3.5×10^4 . An excellent correlation is obtained. The one point which is off has a zero-shear viscosity so close to η_c that an error in either one is magnified manifold.

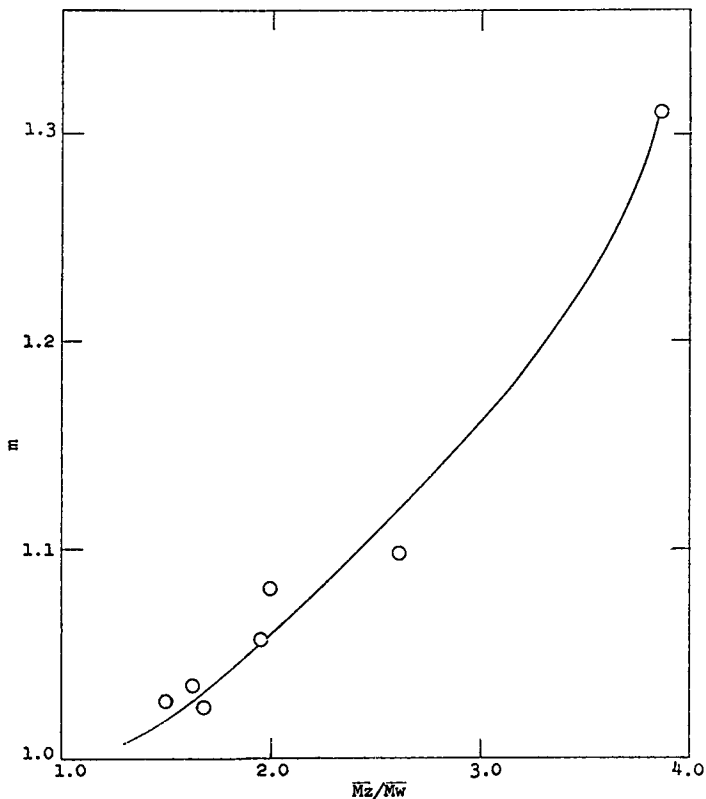


Fig. 5. Molecular weight distribution relationships for polyisobutylene.

Polyisobutylene

The data of Leaderman, Smith, and Williams¹² were used. The slope m was calculated for a shear stress of 10^5 dynes/cm.² and a critical viscosity at 30°C. of 9×10^3 poises and plotted, in Figure 5, against the ratio \bar{M}_z/\bar{M}_w (z -average molecular weight/weight-average molecular weight). One point is not shown ($m = 3.44$; $\bar{M}_z/\bar{M}_w = 4.17$). The agreement is very good.

Polyethylene

The same series of resins previously studied¹ was re-examined and data plotted in Figure 6. The critical viscosity for entanglement at 190°C. was taken to be 39.8 poises. The scatter here is greater than in the previous two instances and may be attributed to errors in the determination of \bar{M}_w and \bar{M}_n . The resins used in Figure 2 are shown with other polyethylene samples in Figure 7. The molecular weight distribution factor shown on the abscissa is from the method previously reported.¹ The agreement between these altogether different rheological methods is very good.

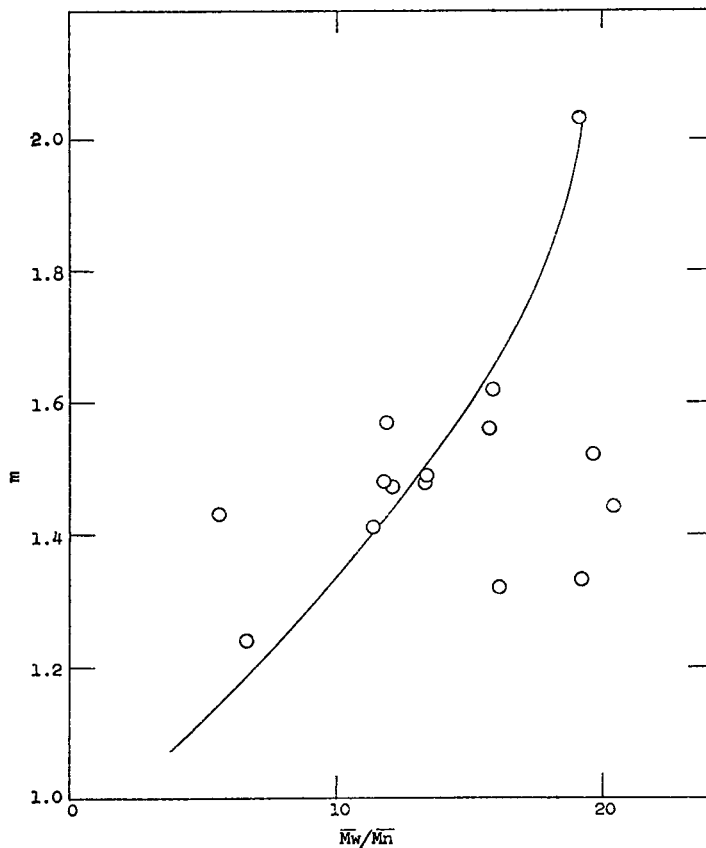


Fig. 6. Molecular weight distribution relationships for polyethylene.

DISCUSSION

The results reported in Figures 2 and 3 and the interpretation given indicate that the critical molecular weight for entanglement is independent of shear stress but not of shear rate.

The slope of the apparent viscosity-molecular weight plot is proportional to the molecular weight distribution, as shown in Figures 4-7. This suggests a method for determining the rheological molecular weight distribution factor by a two-point determination in the non-Newtonian region of shear response according to the following ratio

$$m_1/m_2 = \log (\eta_2/\eta_c)/\log (\eta_1/\eta_c) \quad (2)$$

which can be derived from eq. (1) for two shear stresses (1.78×10^6 and 3.55×10^5 dynes/cm.²). This ratio is plotted in Figure 8 as in Figure 7. These data are single-point determinations. If duplicate runs were made, the scatter would be reduced to a negligible range. As is, the agreement between these two altogether different rheological methods for determining

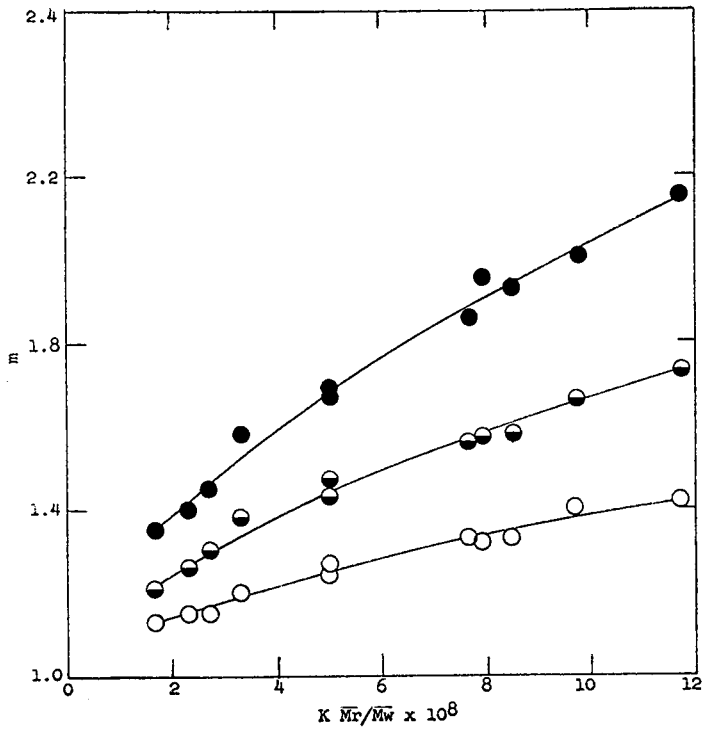


Fig. 7. Molecular weight distribution relationships at three shear stresses for polyethylene.

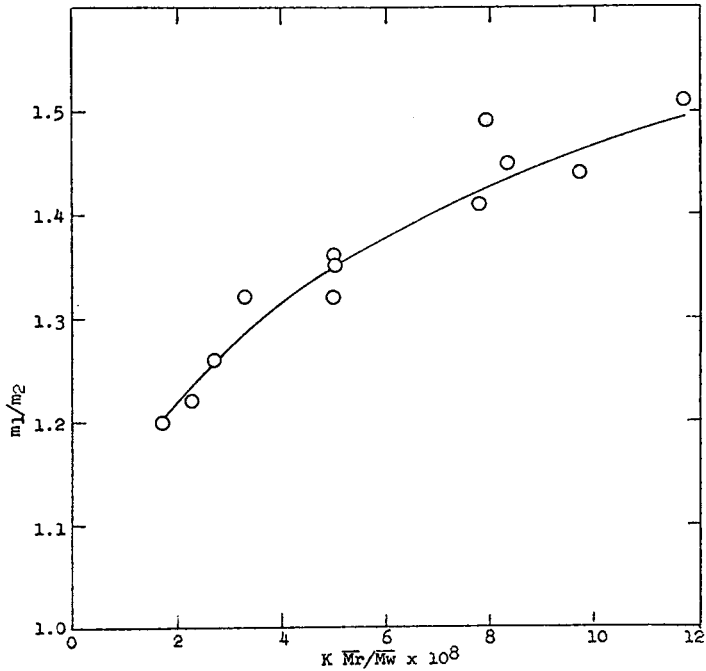


Fig. 8. Two-point determination of the molecular weight distribution from data in the non-Newtonian flow region.

the molecular weight distribution is excellent. Except for actual experimental data no information is common to the calculations involved in the two methods.

This new method suffers from one deficiency. The closer the melt viscosity is to the critical viscosity for entanglement, the more critical is the accuracy required. For the determination of η_c , especially in the case of polyolefins, fractions should be used in order to remove the influence of the molecular weight distribution.

The slope m for broad molecular weight distribution polyethylenes would appear to be relatively insensitive to molecular weight fractions below \bar{M}_c to the extent that they do not entangle.

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Résumé

On expose une nouvelle méthode rhéologique pour la détermination de la distribution du poids moléculaire de polymères qui utilise la viscosité critique pour l'enroulement en même temps que la viscosité Newtonienne et la viscosité apparente à une force de cisaillement dans la région non-Newtonienne. On a employé alternativement deux forces de cisaillement dans la région non-Newtonienne. On a établi que le poids moléculaire critique pour l'enroulement est indépendant de la force de cisaillement mais dépend de la vitesse de cisaillement.

Zusammenfassung

Es wurde eine neue rheologische Methode zur Bestimmung der Molekulargewichtsverteilung von Polymeren entwickelt. Dabei wird die kritische Viskosität für die Verschlingung zusammen mit der Newtonschen Viskosität und der scheinbaren Viskosität bei einer im nicht-Newtonischen Gebiet liegenden Schubspannung verwendet. Andererseits können auch zwei Schubspannungen im nicht-Newtonischen Bereich verwendet werden. Es wurde nachgewiesen, dass das kritische Molekulargewicht für die Verschlingung zwar von der Schubspannung unabhängig, von der Scherungsgeschwindigkeit jedoch abhängig ist.

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