

Effect of Molecular Weight Distribution on Viscosity of Polymeric Fluids

STANLEY MIDDLEMAN, *Department of Chemical Engineering,
University of Rochester, Rochester, New York*

Synopsis

Bueche's theory is modified to account for the effect of polydispersity on viscosity of polymeric fluids. Results indicate that the ratio of weight-average to number-average molecular weight, $\langle M_w \rangle / \langle M_n \rangle$, though a common measure of polydispersity, is insufficient to account completely for the effect of polydispersity on viscosity.

It is possible to predict the non-Newtonian flow curve of a solution of high polymer from molecular theories such as that of Bueche.¹ Bueche's theory is well within order of magnitude agreement with experimental data for polyisobutylene,² polystyrene,³ poly(methyl methacrylate),⁴ poly(acrylic acid),⁵ carboxymethyl cellulose,⁶ polyethylene,⁷ and numerous other materials. Examined in greater detail, however, the evidence would seem to indicate that variations in molecular weight distribution are not adequately accounted for by Bueche's theory.^{3,8} This is not surprising, in view of the fact that the theory assumes all molecules to be identical in length, and so to constitute a monodisperse system.

The general indication is that polydispersity causes a fluid to deviate from Newtonian behavior at a lower shear rate (when referred to equal values of concentration, temperature, zero-shear viscosity, and average molecular weight) than a monodisperse sample, and to show a more gradual rate of decrease of viscosity with shear rate. The purpose of this note is to modify Bueche's development and present a theory from which the quantitative effect of the molecular weight distribution on the flow curve may be determined.

It should be stated at this point that the use of Bueche's theory is illustrative, and does not imply a belief that the theory is quantitatively valid for a monodisperse polymer. One could just as well proceed with the discussion to follow by using theories due, for example, to Rouse⁹ or Pao,¹⁰ or Graessley.¹¹ The point is that even the qualitative failure of these theories is commonly ascribed to the effect of molecular weight distribution. By investigating this feature of the problem one might hope to learn whether other aspects of polymer structure and interaction are of potential significance, and therefore deserving of significant research effort.

Theory

Bueche determines the increase in viscosity per unit volume of solvent due to the presence of a single molecule. An intermediate result is

$$\Delta\hat{\eta} = \widehat{\eta} - \eta_s = (fa^2N^2/36)\{F(\tau_1\dot{\gamma})\} \text{ (per molecule/volume)} \quad (1)$$

where τ_1 is a relaxation time given by

$$\tau_1 = fa^2N^2/3\pi^2kT \quad (2)$$

Here N represents the number of monomer units per molecule (degree of polymerization), a is the distance between monomer units, and f is a molecular friction coefficient. The solvent viscosity is η_s , k is the Boltzmann constant, and T is absolute temperature. The function $F(\tau_1\dot{\gamma})$ is a series of the form

$$F(x) = 1 - \frac{6}{\pi^2} \sum_{n=1}^N \frac{x^2}{n^2(n^4 + x^2)} \left(2 - \frac{x^2}{n^4 + x^2} \right) \quad (3)$$

The molecular weight M may be introduced through the molecular weight of a monomer unit m to give $M = Nm$, and

$$\begin{aligned} \Delta\hat{\eta} &= (fa^2M^2/36m^2)F(\tau_1\dot{\gamma}) \\ \tau_1 &= fa^2M^2/3\pi^2m^2kT \end{aligned} \quad (4)$$

Now we define a continuous distribution function for molecular weight $\phi(M)$, such that the fraction of molecules having molecular weights in the range M to $M + dM$ is $\phi(M)dM$. By its definition

$$1 = \int_0^\infty \phi(M)dM \quad (5)$$

and

$$\langle \mathfrak{F} \rangle = \int_0^\infty \mathfrak{F}(M)\phi(M)dM \quad (6)$$

where \mathfrak{F} is any function of M , and $\langle \mathfrak{F} \rangle$ denotes its average value.

If ν is the number of molecules per unit volume of solution, then the number of molecules (per unit volume) having molecular weights in the range M to $M + dM$ is $\nu\phi(M)dM$. If the increase in viscosity per molecule/volume is multiplied by this quantity one finds the increase in viscosity due to molecules of molecular weight M . By assuming that the viscosity increase due to molecules of different molecular weights may be summed (integrated) over the range of molecular weights to give the total increase in viscosity, one finds

$$\eta - \eta_s = \int_0^\infty (\nu fa^2M^2/36m^2)F(\tau_1\dot{\gamma})\phi(M)dM \quad (7)$$

Since $F(0) = 1$, and $\nu fa^2/m^2$ is supposedly independent of M , one finds, in the limit of vanishing shear rates,*

$$\eta_0 - \eta_s = (\nu fa^2/36m^2) \int_0^\infty M^2\phi(M)dM = \nu fa^2\langle M^2 \rangle/36m^2 \quad (8)$$

Thus $fa^2/m^2 = 36(\eta_0 - \eta_s)/\nu\langle M^2 \rangle$ and one may write

$$(\eta - \eta_s)/(\eta_0 - \eta_s) = \int_0^\infty M^2F(\tau_1\dot{\gamma})\phi(M)dM/\langle M^2 \rangle \quad (9)$$

where

$$\tau_1 = \frac{12}{\pi^2} \frac{M^2}{\langle M^2 \rangle} \frac{(\eta_0 - \eta_s)}{\nu kT}$$

The mass concentration c is related to the number density ν by

$$c = \nu\langle M \rangle/N_0 \quad (10)$$

where N_0 is Avogadro's number.

Commonly used molecular weight averages are the number-average,

$$\langle M_n \rangle = \int_0^\infty M\phi(M)dM = \langle M \rangle \quad (11)$$

and the weight-average,

$$\begin{aligned} \langle M_w \rangle &= \int_0^\infty M^2\phi(M)dM/\langle M_n \rangle \\ &= \langle M^2 \rangle/\langle M_n \rangle \end{aligned} \quad (12)$$

In terms of these averages our modification of Bueche's theory becomes

$$(\eta - \eta_s)/(\eta_0 - \eta_s) = \int_0^\infty M^2F(\tau_1\dot{\gamma})\phi(M)dM/\langle M_w \rangle\langle M_n \rangle \quad (13)$$

$$\begin{aligned} \tau_1 &= \frac{12}{\pi^2} \frac{M^2}{\langle M_w \rangle\langle M_n \rangle} \frac{\langle M_n \rangle(\eta_0 - \eta_s)}{cRT} \\ &= \langle \tau_1 \rangle_n \frac{M^2}{\langle M_w \rangle\langle M_n \rangle} \end{aligned} \quad (14)$$

where $\langle \tau_1 \rangle_n$ represents a relaxation time based on the number-average molecular weight.

We note that similar results may be found in the works of Peticolas¹² and Menefee and Peticolas.¹³ These workers considered the theory of Zimm¹⁴ rather than that of Bueche, and most of their results are in terms of a weight fraction distribution function, rather than the number fraction used here.

*In effect this begs the question of the validity of the theory at low shear rates. The result is that molecular constants such as f and a are replaced by bulk properties of the solution.

More important, however, is the fact that they did not investigate the quantitative dependence of viscosity curves on the shape of the distribution function.

Equation (13) is the result sought: it gives $\eta(\dot{\gamma})$ as a function of $\phi(M)$. Before turning to some numerical examples it is possible to draw an inference about the general effect of $\phi(M)$ on the viscosity curve. The M^2 term in eq. (13) is an indication that the viscosity will be more affected by the high end of the molecular weight distribution than the low end. This is in agreement with a recent observation of Nakajima and Wong¹⁵ on polyethylene blends. They found that the addition of high molecular weight material to a sample appreciably affected the shape of the flow curve, while the curve was much less affected by the addition of low molecular weight material.

Numerical Examples

Equation (13) has been integrated numerically to illustrate the shape of the viscosity curve for various molecular weight distributions. As an illustrative example we took a form of distribution function given by eq. (15):¹⁶

$$\phi(M) = [B^A/\Gamma(A)]M^{A-1}e^{-BM} \quad (15)$$

where $\Gamma(A)$ represents the Gamma function.

The constants A and B are determined from two average molecular weight determinations. For example,

$$\langle M_n \rangle = A/B \quad (16)$$

$$\langle M_w \rangle = (A + 1)/B \quad (17)$$

A measure of the breadth of the molecular weight distribution is

$$\langle M_w \rangle / \langle M_n \rangle = (A + 1)/A \quad (18)$$

The larger the value of $\langle M_w \rangle / \langle M_n \rangle$, the broader is the molecular weight distribution.

Figure 1 illustrates a few numerical results for the distribution function defined in eq. (15). The curves vary with $\langle M_w \rangle / \langle M_n \rangle$ in the manner commonly observed.

One source of controversy in the use of reduced variable plots lies in the question of which molecular weight average should be used in the calculation of an average relaxation time, $\langle \tau_1 \rangle$.^{4,16}

It is possible to show viscosity curves using different definitions of $\langle \tau_1 \rangle$, since eq. (14) could be rewritten as

$$\tau_1 = \langle M^2 / \langle M_w \rangle \langle M_x \rangle \rangle \langle \tau_1 \rangle_x \quad (19)$$

where $\langle \tau_1 \rangle_x$ is a relaxation time based on any molecular weight average, $\langle M_x \rangle$. Actually, such curves are obtained by shifting the curves of Figure 1

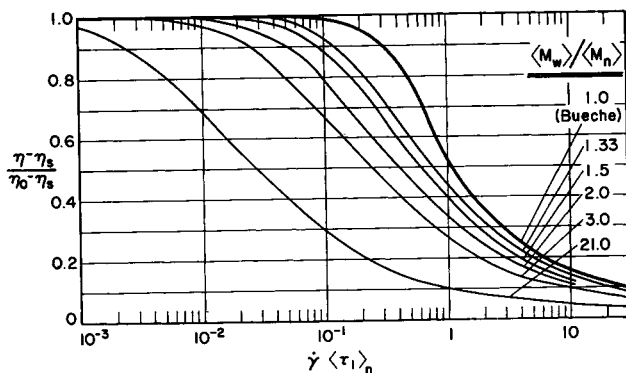


Fig. 1. Theoretical flow curves for material with distribution function of eq. (15). Relaxation time based on number-average molecular weight.

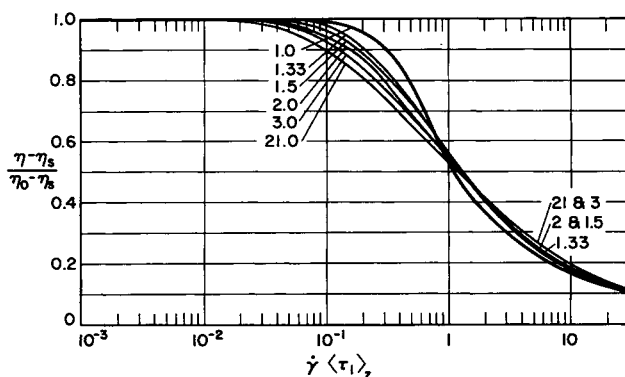


Fig. 2. Fig. 1 replotted by basing relaxation time on Z-average molecular weight.

by the factor $\langle M_z \rangle / \langle M_n \rangle$. Figure 2 shows the result of basing the relaxation time on the Z-average molecular weight,

$$\langle M_z \rangle = \frac{\langle M^3 \rangle}{\langle M^2 \rangle} \tag{20}$$

while Figure 3 shows the same curves plotted for a relaxation time based on the $(Z + 1)$ -average molecular weight,

$$\langle M_{z+1} \rangle = \langle M^4 \rangle / \langle M^3 \rangle \tag{21}$$

Brodnyan and Kelley¹⁶ offer evidence that the relaxation time should be based on the $(Z + 1)$ -average, but also point out that different averages than this are appropriate at low concentration, and at high shear rate. Our results indicate that the higher averages do tend to compress the differences among various curves, but not equally at all shear rates. Furthermore, neither of these average relaxation times forces the curves of polydisperse systems to come especially close to Bueche's theoretical curve.

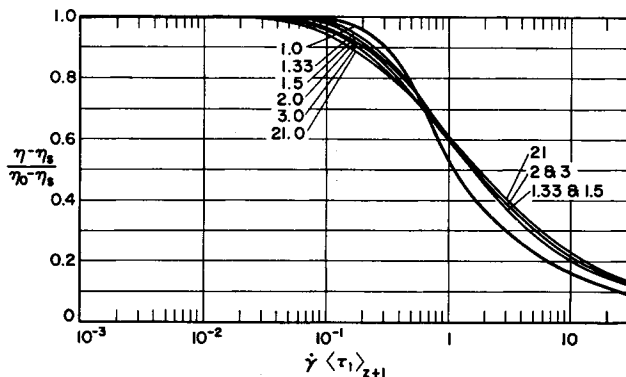


Fig. 3. Fig. 1 replotted by basing relaxation time on $(Z + 1)$ -average molecular weight.

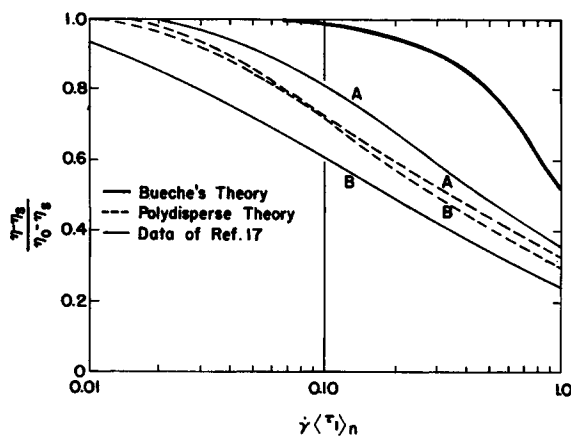


Fig. 4. Comparison of theory with experimental data¹⁷ for two polydisperse samples of polyisobutylene.

Undoubtedly, no single average of molecular weight will be sufficient to allow a unique reduced variable correlation to describe precisely the viscosity curves of a wide class of materials, in view of the fact that the curves are sensitive to the shape of the molecular weight distribution, for which $\langle M_w \rangle / \langle M_n \rangle$ is not a unique measure, in general.

Indeed, Porter et al.¹⁷ present data for solutions of polyisobutylene which show clearly that the viscosity curves do not always rank according to $\langle M_w \rangle / \langle M_n \rangle$, but instead are appreciably affected by the tail of the molecular weight distribution function. We have taken their measured molecular weight distribution functions and predicted $(\eta - \eta_s) / (\eta_0 - \eta_s)$ versus $\dot{\gamma} \langle \tau_1 \rangle_n$ with the results shown in Figure 4. The correspondence between theory and experiment is poor.

Closer examination indicates a possible reason for this poor agreement. One does not expect these non-Newtonian molecular theories to be valid except for molecular weights above the entanglement molecular weight, M_e .

If M_e for bulk polyisobutylene is taken as 17,000,¹⁸ and if the product of M_e and volume fraction of polymer is taken to be 17,000 for solutions,⁸ then one finds M_e for the 45% solution used by Porter et al.¹⁷ to be approximately 35,000. The distribution function for the polymers studied indicates that about half the total number of molecules of each polymer were of molecular weight less than M_e . Hence one must be careful in applying such theories to polydisperse systems even when $\langle M_w \rangle > M_e$. A more proper restriction would be that $\langle M_w \rangle$ should probably be at least an order of magnitude greater than M_e in order to apply theories such as Bueche's to polydisperse polymers.

It is unfortunate that the data examined represent the only example of a complete distribution curve accompanied by a complete viscosity curve known to the author. As more such data become available one might hope for a more significant test of the ideas presented here.

Another significant failure of these theories may lie in our ignorance of polymer-solvent interaction and of polymer-polymer interaction. Indeed, one might express surprise that the theories work as well as they do, in view of the fact that such interaction is not built into the molecular analyses. In fact, however, the device of replacing the frictional parameter f by bulk properties at zero shear rate [as illustrated in going from eq. (8) to eq. (9)] has the effect of introducing the major consequences of interaction into the theory explicitly through the zero-shear viscosity, η_0 . One might suppose that this interaction between polymer and solvent, and among polymer molecules in concentrated solutions and melts, is itself a function of shear rate and concentration, and varies from one polymer-solvent system to another in a manner beyond our ability to describe at the present time.

References

1. F. Bueche, *J. Chem. Phys.*, **22**, 1570 (1954).
2. J. Dunleavy and S. Middleman, *Trans. Soc. Rheol.*, **10**:1, 157 (1966).
3. R. L. Ballman and R. Simon, *J. Polymer Sci.*, **2**, 3557 (1964).
4. J. G. Brodnyan, R. H. Shoulberg, and E. L. Kelley, *SPE Trans.*, **4**, 277 (1964).
5. J. G. Brodnyan and E. L. Kelley, *Trans. Soc. Rheol.*, **5**, 205 (1961).
6. J. Schurz, *J. Colloid Sci.*, **14**, 492 (1959).
7. J. M. McKelvey, *Polymer Processing*, Wiley, New York, 1962, p. 36.
8. R. S. Porter and J. F. Johnson, *Trans. Soc. Rheol.*, **7**, 241 (1963).
9. P. E. Rouse, Jr., *J. Chem. Phys.*, **21**, 1272 (1953).
10. Y. H. Pao, *J. Chem. Phys.*, **25**, 1294 (1956); *J. Appl. Phys.*, **28**, 591 (1957).
11. W. W. Graessley, *J. Chem. Phys.*, **43**, 2696 (1965).
12. W. L. Peticolas, *J. Chem. Phys.*, **35**, 2128 (1961).
13. E. Menefee and W. L. Peticolas, *J. Chem. Phys.*, **35**, 946 (1961).
14. B. N. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).
15. N. Nakajima and P. S. L. Wong, *Trans. Soc. Rheol.*, **9**, 3 (1965).
16. J. G. Brodnyan and E. L. Kelley, *Trans. Soc. Rheol.*, **7**, 125 (1963).
17. R. S. Porter, M. Cantow, and J. F. Johnson, in *Proc. 4th Intern. Congr. Rheol.*, Part 2, E. H. Lee, Ed., Interscience, New York, 1965, p. 479.
18. R. S. Porter and J. F. Johnson, in *Proc. 4th Intern. Congr. Rheol.*, Part 2, E. H. Lee, Ed., Interscience, New York, 1965, p. 467.

Résumé

La théorie de Bueche est modifiée pour rendre compte de l'effet de la polydispersité sur la viscosité de fluides polymériques. Les résultats indiquent que le rapport du poids moléculaire moyen au poids moléculaire moyen en nombre $\langle M_w \rangle / \langle M_n \rangle$, bien qu'étant une commune mesure de polydispersité est insuffisant pour rendre compte complètement de l'effet de la polydispersité sur la viscosité.

Zusammenfassung

Die Theorie von Bueche wird zur Berücksichtigung des Einflusses der Polydispersität auf die Viskosität von Polymerflüssigkeiten modifiziert. Die Ergebnisse zeigen, dass das Verhältnis von Gewichtsmittel zu Zahlenmittel des Molekulargewichts $\langle M_w \rangle / \langle M_n \rangle$, das gemeinhin als Mass für die Polydispersität benutzt wird, doch zu einer vollständigen Erfassung des Einflusses der Polydispersität auf die Viskosität nicht ausreicht.

Received March 17, 1966

Prod. No. 1468