Polymer Rheology: Influence of Molecular Weight and Polydispersity

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Synopsis

Literature data on the non-Newtonian flow of bulk polymer and of polymer solutions are correlated on the basis of a four-parameter equation, $\eta = \eta_\infty + (\eta_0 - \eta_\infty)/[1 + (\tau D)^m]$, η being the viscosity at shear rate D, and η_0 and η_∞ limiting values at $D = 0$ and $D = \infty$, respectively. The parameters η_0, η_∞, and τ all show dependence on molecular weight, and in general there is good correlation between τ and η_0. There is evidence that τ is related to a molecular weight higher than the weight-average. The exponent m shows dependence on molecular weight distribution and approaches an upper limit of unity for a monodisperse linear polymer. For linear unblended polymers it may be expressed empirically by $m = (\bar{M}_n/\bar{M}_w)^{1/5}$.

Introduction

It is widely recognized that polydispersity is an important factor in rheological behavior and can have a significant influence on the flow curve of a non-Newtonian fluid. The subject has recently been reviewed by Schurz,[1] who observes that in general polydispersity acts in such a way as to broaden the flow curves and render them more flat. Other workers have referred to the influence on the onset of non-Newtonian flow, while Dunleavy and Middleman[2] have recently observed that "it does seem clear that polydispersity is a variable not properly accounted for in any theoretical or experimental work to date" (1966).

In previous work[3] it has been shown that the flow curves for a wide range of pseudoplastic systems can be represented by an equation of the form

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)/(1 + aD^m)$$
$$= \eta_\infty + (\eta_0 - \eta_\infty)/[1 + (\tau D)^m] \tag{1}$$

where η is the viscosity at shear rate D, and η_0 and η_∞ are limiting values at $D = 0$ and $D = \infty$, respectively. τ is a constant such that at a shear rate τ^{-1} the viscosity of the system assumes the mean value $(\eta_0 + \eta_\infty)/2$.

The notation here is slightly different from that originally used, the shear rate exponent being denoted by m in order to avoid possible confusion with the power law relation, where shear stress is proportional to the nth

power of the shear rate. According to eq. (1) a graph of log $(\eta - \eta_\infty)$ against log D will be linear at high rates of shear,[3] with a slope $-m$. A very approximate relationship between the two exponents is thus indicated, $m \approx 1 - n$.

Equation (1) was originally derived from a consideration of particle interactions in a disperse system, but in practice it was found that with a fixed value of $2/3$ for the exponent m it also gave a good representation of data for polymer solutions and melts,[3-6] i.e., the equation has been widely used in the form

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)/[1 + (\tau D)^{2/3}] \tag{2}$$

However this exponent does not appear to be universally applicable, and in some cases higher values have been used.[7] Gillespie[8] has found that for "monodisperse" polystyrenes eq. (2) does not give a satisfactory representation but a good description is given by the Williamson equation,[9]

$$\eta = \eta^* + C_1/(C_2 + D) \tag{3}$$

where η^* is the equilibrium viscosity due to hydrodynamic effects and C_1 and C_2 are constants.

Again, for broad distributions, Gillespie finds that eq. (3) is inadequate. He concludes that eqs. (2) and (3) are each of limited application and derives a more general flow equation involving a ratio (α) of maximum and minimum relaxation times.

He finds that $10 > \alpha > 1$ gives curves which are practically identical to those of eq. (3), while $\alpha = 300 \pm 100$ gives close agreement with eq. (2).

Inspection of eqs. (2) and (3) suggests an alternative approach. The two equations are essentially of the same form and may be regarded as special cases of eq. (1), with $m = 2/3$ and $m = 1$, respectively. Equation (1) may therefore be regarded as a general equation in which the exponent m is an adjustable parameter related to polydispersity. Reducing the exponent gives a broadening of the curves as indicated in Figure 1.

Powell[10] has in fact introduced empirical equations for polymer systems which are essentially similar to eq. (1) and with an exponent which is postulated to be a function of molecular weight distribution. For a bulk polymer, Powell's equation takes the form

$$\eta = \eta_0/[1 + (\tau D)^{2F}] \tag{5}$$

where τ is a representative relaxation time, $F = (\bar{M}_n/\bar{M}_w)^x$, M_n is the number-average molecular weight, $\bar{M}_w$ is the weight-average molecular weight, and x is a constant related to molecular shape. For a monodisperse system $F = 1$.

Equation (5) is effectively a special case of eq. (1), with $\eta_\infty = 0$. For a polymer solution Powell uses a different equation, but this again can be regarded as a special case of eq. (1) in which η_∞ is identified with the solvent viscosity, η_s (assumed to be independent of rate of shear).
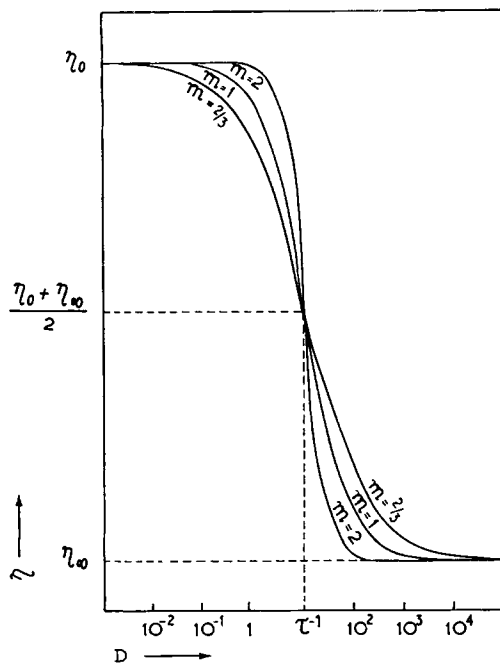
Fig. 1. Theoretical curves. $\eta = \eta_\infty + (\eta_0 - \eta_\infty)/[1 + (\tau D)^m]$. Effect of exponent m.

If m is regarded as an adjustable parameter, eq. (1) provides a means of rheological characterization in terms of four (not necessarily independent) parameters, η_0, η_∞, τ, and m. For a linear polymer it should be possible to relate these quantities to molecular weight, molecular weight distribution (polydispersity), and temperature. With this object in view an analysis has been undertaken of published rheological data on polymers of known molecular weight distribution.

Evaluation of Flow Parameters

For a known value of the exponent m, graphical methods for evaluating the parameters η_0, η_∞, and τ of eq. (1) have been fully described elsewhere.[3] At sufficiently low rates of shear a plot of $1/\eta$ against D^m should be linear. Such a plot generally serves both to establish the value of m and to evaluate the constants η_0 and τ. The intercept is $1/\eta_0$ and the slope a/η_0, where $a = \tau^m$. The correctness of the exponent m can subsequently be verified from a second graph of η against $(\eta_0 - \eta)D^{-m}$, which should be linear over a wider range. The intercept of this second graph is η_∞.

Polystyrene Melts

Extensive rheological data has been published on polystyrene melts, particularly on polymers of narrow molecular weight distribution[11-14]

prepared by anionic polymerization. Rudd[11] has published capillary rheometer data at 500°K on six such polymers, with $\bar{M}_w/\bar{M}_n$ in the range 1.04–1.08. On applying eq. (1), plots of $1/\eta$ against D were found to be linear at low rates of shear, as in Figure 2, indicating an exponent of unity. Figure 3 shows a second graph of η against $(\eta_0 - \eta)D^{-1}$ for polymer S105, which remains linear over the whole range, in confirmation of the value of m. The intercept of this graph is η_∞, and since this is finite it is evident that Powell's equation is not applicable.

With an exponent of unity, literature data on anionic polymers[11–14] were correlated on the basis of eq. (1). The molecular weight dependence of η_0 and η_∞ follows the general pattern of behavior observed in polymer systems by Porter and Johnson[15] and by Hoffmann and Rother,[16] i.e., η_∞ increases with molecular weight but much less abruptly than the 3.4 power dependence shown by η_0. The parameter τ also increases with molecular weight but the ratio η_0/τ shows little dependence on either molecular weight or temperature. It is interesting to compare this behavior with the findings of Tobolsky et al.[17,18] from creep and stress relaxation measurements on the anionic polymers examined in melt flow by Rudd[11] and Stratton.[12] Tobolsky demonstrated the existence for "monodisperse" polystyrene of a sharply defined maximum relaxation time (τ_m) and employed procedure X to evaluate both τ_m and the tensile viscosity (η_t). It was established that the ratio η_t/τ_m was almost independent of molecular weight. Assuming that the system is isotropic and has a Poisson ratio of 0.5 the shear viscosity (which can be identified with η_0) will equal one third
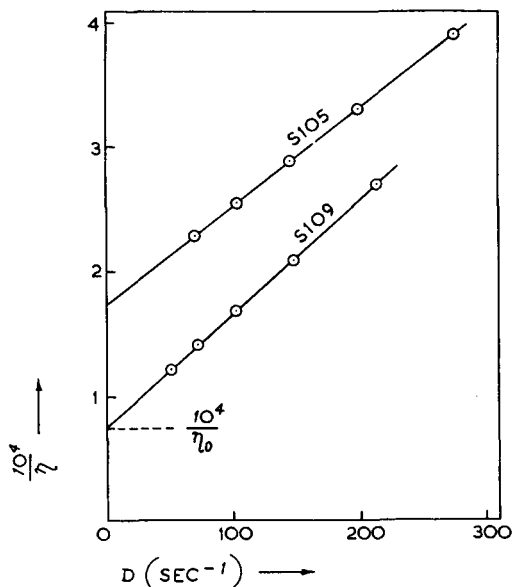

Fig 2. Narrow distribution polystyrenes. Graphical evaluation of η_0 and τ.
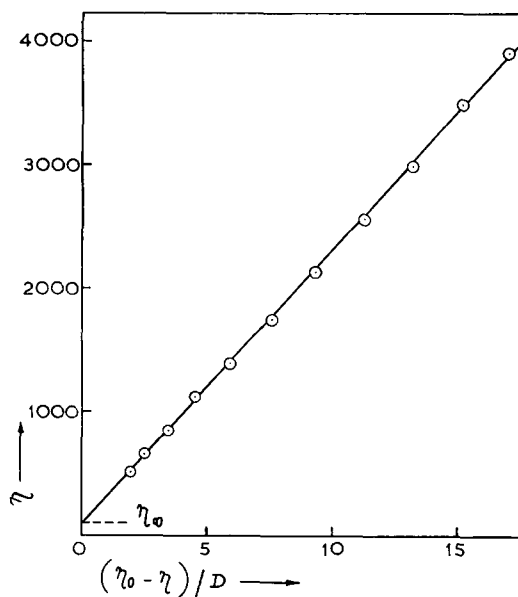
Fig. 3. Flow data for a typical anionic polystyrene[11] (S105) plotted in accordance with eq. (1), with an exponent of unity.

the tensile viscosity. Correspondence between the parameter τ derived from the melt flow data and Tobolsky's maximum relaxation time (τ_m) is indicated in Figure 4, where the two quantities are combined in a single graph against η_0. Tobolsky's viscosity values are of the order 10^{13}–10^{15} P, indicative of the glassy state, and Figure 4 indicates an approximate proportionality between viscosity and relaxation time extending over twelve
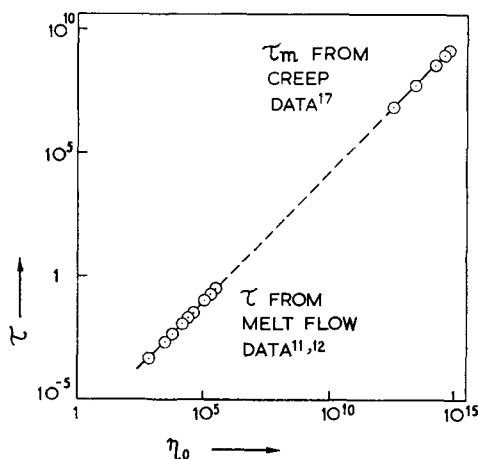

Fig. 4. Comparison of melt flow[11,12] and creep[17] data for anionic polystyrenes.

decades and passing through the glass transition temperature. Earlier work by Andrews and Tobolsky[19] on polyisobutene may also be recalled, in which it was found that the two parameters η_t and τ_m showed a very similar temperature and molecular weight dependence, both quantities varying approximately as the molecular weight to the power of 3.3.

Rudd[11] has also given data for an isothermal polystyrene with a broader distribution ($\bar{M}_w/\bar{M}_n \approx 2$). This required a lower exponent (0.88) and gave a significantly lower value for the ratio η_0/τ.

Polybutadiene Melts

A similar analysis was carried out on capillary rheometer data by Gruver and Kraus[20,21] on two different types of polybutadienes: (a) n-butyllithium-polymerized polybutadienes with a very narrow molecular weight distribution and (b) one group (class 1) of cis-polybutadienes prepared by the Phillips process in which $\bar{M}_w/\bar{M}_n$ is believed to lie between 2 and 4 and there is some degree of long chain branching.

A comparison of the two types showed the following features. (1) For the "monodisperse" polymers, the shear rate exponent was unity; for the broader distribution cis-polymers the exponent was $^2/_3$. This value may be influenced by branching as well as by polydispersity. (2) In each system the ratio η_0/τ was virtually independent of either molecular weight or temperature. (3) In a composite plot of η_0 against viscosity-average molecular weight points for the two different systems were colinear, i.e., in spite of the different distributions there was a close correlation between η_0 and $\bar{M}_v$. (4) A composite plot of log τ against log $\bar{M}_v$ gave two parallel lines, the broader distribution cis-polybutadienes showing significantly higher values of τ than monodisperse polymers of the same $\bar{M}_v$. This suggests that τ may be related to a higher moment of the distribution curve.

Additional data by Boyce et al.[22] on lower molecular weight monodisperse polybutadienes can also be represented with an exponent of unity.

Polymer Solutions

Porter and Johnson[23,24] have published viscosity–shear data on moderately concentrated solutions of polyisobutene in cetane. For a narrow fraction with $\bar{M}_w/\bar{M}_n \approx 1.03$ the solution data can be represented with an exponent of unity. Comparable data for solutions with a broader distribution ($\bar{M}_w/\bar{M}_n \approx 3$) gave a lower exponent (0.8). It thus appears that for linear polymers, either in bulk or in concentrated solution, polydispersity has the effect of lowering the shear rate exponent.

Polypropylene Melts

van der Vegt[25] has published viscosity–shear data on a series of polypropylene melts differing in both molecular weight and in molecular weight distribution, with $Q = \bar{M}_w/\bar{M}_n$ ranging from 3.5 to 25.

For these polymers η_∞/η_0 appears to be very small and the evaluation of the exponent m is correspondingly easy. Equation (1) can be written in the form

$$\eta/\eta_0 = \eta_\infty/\eta_0 + (1 - \eta_\infty/\eta_0)/[1 + (\tau D)^m] \qquad (1a)$$

If $\eta_\infty/\eta_0 \ll 1$, a graph of log $(\eta_0/\eta - 1)$ against log D will be linear, as suggested by Powell,[10] and the gradient will be m. The effect of distribution on the gradient is shown in Figure 5; polydispersity has the effect of lowering the exponent, as in the other polymer systems examined.

The analysis showed the following additional features. For the different distributions there is little or no correlation between η_0 and τ. No molecular weights are specified by van der Vegt but to a first approximation $\bar{M}_v$ is proportional to $\eta_0^{0.3}$. A graph of τ against $\eta_0^{0.3}$ indicated little correlation between τ and $\bar{M}_v$. In order to simulate a higher molecular weight, τ was replotted against the product $\eta_0^{0.3}Q^{0.5}$. This gave a very reasonable correlation.

Polymer Blends

Ballman and Simon[13] have published flow data on anionic polystyrenes both separately and in bimodal blends. With an exponent of 0.75, eq. (1) gives an excellent representation of the blend data.

In Figure 6 values of τ for both "fractions" and blends are plotted against $\bar{M}_w$ and against $\bar{M}_z$. It is evident that $\bar{M}_z$ gives a much better correlation

Discussion

Although eq. (1) involves four parameters it appears that three of these, η_0, η_∞, and τ, are related, in so far as each is a function of molecular weight
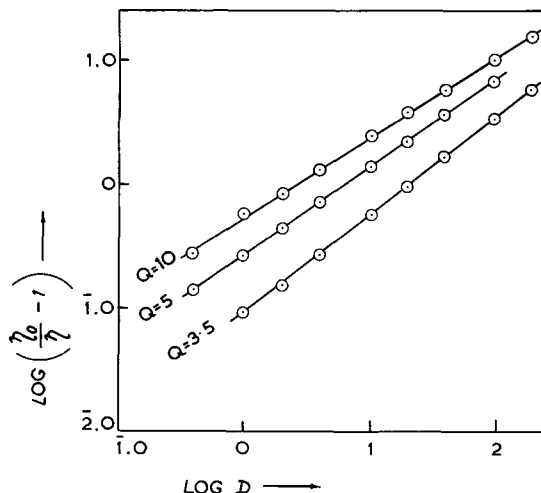

Fig. 5. Polypropylene melts.[25] Effect of molecular weight distribution on shear rate exponent.
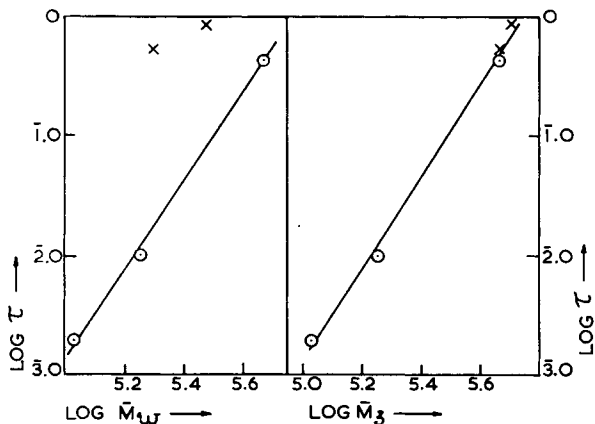
Fig. 6. τ related to molecular weight for ($\odot$) polystyrene "fractions" and ($\times$) bimodal blends.

and temperature. In general there is a good correlation between η_0 and τ, as would be expected if τ is a relaxation time related to chain mobility. For anionic polystyrenes, comparison with Tobolsky's creep data[17] suggests that τ may represent the maximum relaxation time of the system.

Evidence on polystyrene, polybutadiene, and polypropylene strongly indicates that while η_0 is related to $\bar{M}_w$ or $\bar{M}_v$, τ is dependent on a higher moment of the distribution curve. Accordingly, if polymers differ materially in molecular weight distribution, as in the polypropylenes of van der Vegt,[25] the correlation between η_0 and τ is obscured. It is possible that τ may be related to $\bar{M}_z$, but further information is required on this point.

In earlier work eq. (1) was widely used with a shear rate exponent of $^2/_3$, and from a consideration of viscosity as an even function of rate of shear it was argued that m could, in fact, assume any fractional value p/q where p is even and q odd. However, it is difficult to justify the use of an exponent which varies in such a manner, with a discrete series of admissable values. Indeed a consideration of all possible values of p and q would indicate that this condition does not impose any restriction on the value of m.

The present results indicate that for linear polymers, either in bulk or in concentrated solution, the exponent is a function of molecular weight distribution, with an upper limit of unity for a monodisperse system. There is evidence that the exponent is also influenced by branching. On omitting data which relates to branched polymers or blends, all the results can be represented empirically by the simple relationship

$$m = (\bar{M}_n/\bar{M}_w)^{1/5}$$

In Figure 7 the results for the different polymer systems are shown collectively on this basis. A more general relationship may require a different index of dispersion.
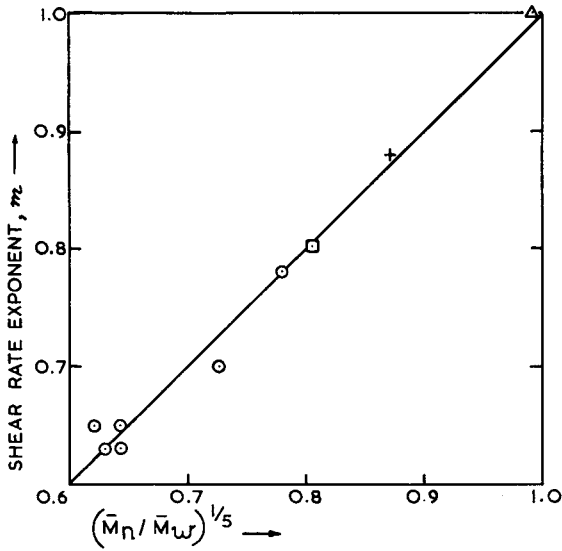
Fig. 7. Empirical relationship, $m = (M_n/M_w)^{1/5}$; accumulated data for various linear polymers: ($\triangle$) "monodisperse" polystyrenes,[11-14] polybutadienes,[20-22] and polyisobutene solutions;[23] ($\odot$) polypropylenes;[25] ($\square$) polyisobutene solutions;[24] ($+$) isothermal polystyrene[11].
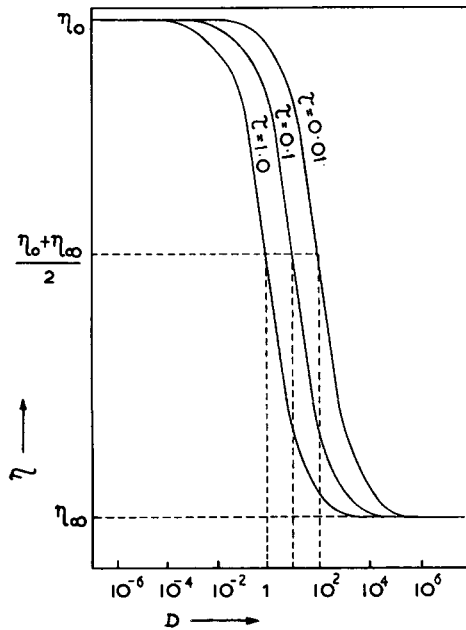

Fig. 8. Simple shift associated with the parameter τ in the equation $\eta = \eta_\infty + (\eta_0 - \eta_\infty)/[1 + (\tau D)^m]$. η_0, η_∞ and m are constant.

This effect of polydispersity on the shear rate exponent is in qualitative agreement with the ideas expressed by Powell,[10] although for a monodisperse system the exponent given by Powell's relationship is not 1, but 2. Ultimately the exponent must be related to a distribution of relaxation times. If a value of unity corresponds to the relaxation spectrum of a monodisperse polymer it is conceivable that a single relaxation time would give a value of 2.

The analysis indicates that polydispersity affects the flow curve in two respects, one associated with the exponent m and the other with the parameter τ. A wider distribution gives a lower value of m and a broadening of the flow curve, as indicated in Figure 1. Also for a given value of $\bar{M}_w$ (and η_0) there will be a higher value of τ, giving a horizontal shift of the η–log D curve, as illustrated in Figure 8, resulting in the onset of non-Newtonian flow at lower rates of shear.

References

1. J. Schurz, Polymer Fractionation, M. R. J. Cantow, Ed., Academic Press, New York, 1967, p. 317.

2. J. E. Dunleavy, Jr., and S. Middleman, Trans. Soc. Rheol., 10, Part 1, 157 (1966).

3. M. M. Cross, J. Colloid Sci., 20, 417 (1965).

4. M. M. Cross, Europ. Polym. J., 2, 299 (1966).

5. H. Schott, Rheol. Acta., 7, 179 (1968).

6. T. Kataoka and S. Ueada, J. Appl. Polym. Sci., 12, 939 (1968).

7. M. M. Cross, S.C.I. Monograph No. 26, Society of Chemical Industry, London, 1967, p. 381.

8. T. Gillespie, J. Colloid Interface Sci., 22, 563 (1966).

9. R. V. Williamson, Ind. Eng. Chem., 21, 1108 (1929).

10. A. Powell, Polymer, 7, 91 (1966).

11. J. F. Rudd, J. Polym. Sci., 44, 459 (1960).

12. R. A. Stratton, J. Colloid Interface Sci., 22, 517 (1966).

13. R. L. Ballman, and R. H. M. Simon, J. Polym. Sci. A, 2, 3560 (1964).

14. D. P. Wyman, L. J. Elyash, and W. J. Frazer, J. Polym. Sci. A, 3, 681 (1965).

15. R. S. Porter and J. F. Johnson, J. Appl. Phys., 32, 2326 (1961).

16. M. Hoffmann and K. Rother, Makromol. Chem., 80, 95 (1964).

17. A. V. Tobolsky, J. J. Aklonis, and G. Akovali, J. Chem. Phys., 42, 723 (1965).

18. A. V. Tobolsky and K. Murakami, J. Polym. Sci., 40, 443 (1959).

19. R. D. Andrews and A. V. Tobolsky, J. Polym. Sci., 7, 221 (1951).

20. J. T. Gruver and G. Kraus, J. Polym. Sci. A, 2, 797 (1964).

21. G. Kraus and J. T. Gruver, J. Appl. Polym. Sci., 9, 739 (1965).

22. R. J. Boyce, W. H. Bauer, and E. A. Collins, Trans. Soc. Rheol., 10, Part 2, 545 (1966).

23. R. S. Porter and J. F. Johnson, Polymer, 5, 201 (1964).

24. R. S. Porter and J. F. Johnson, J. Polym. Sci., 50, 379 (1961).

25. A. K. van der Vegt, Plastics Inst. Trans. Proc., 32, 165 (1964).