A Model Relating the Elastic Properties of High-Density Polyethylene Melts to the Molecular Weight Distribution

B. H. BERSTED, *Research and Development Department, Amoco Chemicals Corporation, Amoco Research Center, Naperville, Illinois 60540*

Synopsis

An earlier model relating the variation of the steady-shear melt viscosity of high-density polyethylene to the molecular weight distribution is applied toward predicting the steady-shear elastic compliance, the first normal stress difference, and relaxation spectrum as a function of shear rate from the molecular weight distribution. The model envisions the cutting off of longer relaxation times as the shear rate is raised such that at any shear rate $\dot{\gamma}$ the molecular weights and their corresponding maximum relaxation times τ_m are partitioned into two classes; the relaxation times are partitioned into operative and inoperative states, depending on whether they are less than or greater than τ_c, the maximum relaxation time allowed at $\dot{\gamma}$. Equations relating molecular weight and relaxation time to the steady-shear elastic compliance and viscosity are assumed valid at nonzero shear rates, except for the partitioning effect of shear rate. The shear rate dependence of the first normal stress difference and the steady-shear viscosity for polyethylene melts is successfully predicted over the range covered by the cone-and-plate viscometer. The assumed proportionality constant between τ_c and $1/\dot{\gamma}$ was determined to be 1.7. Using this relation, the maximum relaxation time at 190°C for a polyethylene molecule of molecular weight M is given by $\tau_m = 1.4 \times 10^{-19} (M)^{3.33}$. Reasonable agreement has been obtained between the experimentally determined relaxation spectrum of a polyethylene melt and that predicted from the molecular weight distribution. The agreement is best at the longest relaxation times.

INTRODUCTION

The elastic properties of polymer melts play a dominant role in polymer processing, particularly in extrudate swelling and unstable flow. Consequently, a fundamental understanding of the relationship of molecular structure to elastic parameters is desirable.

Much progress has been made in the last 10 years toward understanding the effect of molecular parameters on the viscoelastic behavior of polymer melts and solutions. While the specific mechanisms leading to the variation of steady-shear viscosity and elastic parameters with shear rate are still debated, the prevailing view of most authors is that molecular entanglements are the source of both the elasticity and variation of viscosity with shear rate in uncrosslinked high molecular weight polymer melts.[1] Graessley[2,3,4] proposes that the shear rate dependence of the viscosity is due to the variation of entanglement density with shear rate. However, the resulting theory does not directly give insight into precisely how the molecular weight distribution affects viscoelastic behavior.

Shida and Shroff[5] have combined the shear dependence from Graessley's theory with linear viscoelastic data to predict the steady-shear viscosity. However, no direct quantitative connection with molecular weight is demonstrated.

In an earlier publication,[6] the author demonstrated that the steady-shear melt viscosity of high-density polyethylene melts could be directly predicted from the molecular weight distribution. This was accomplished by partitioning all molecular weights present in the sample into two classes; those below the partitioning molecular weight M_c contribute to the viscosity as they do at zero shear, and those above M_c contribute to the viscosity as though they were of molecular weight M_c. M_c is a unique function of shear rate.

In view of the author's successful prediction of melt viscosity, and the prediction by others of relaxation spectra[7,8] and elastic properties[9] from steady-shear viscosity data, the application of the author's model to elastic behavior in polyethylene melts seems justified. This approach is shown to successfully account for the variation of the first normal stress difference with shear rate, and gives a reasonable approximation to the terminal relaxation spectrum.

EXPERIMENTAL

The two polyethylene samples used in this study were made by different experimental processes.

The molecular weight distribution data were obtained at 135°C with four Styragel columns of porosities 10^6, 10^5, 10^4, and 10^3 Å, and calibration was effected using a modified[6] universal calibration procedure.

Capillary rheological data were obtained at 190°C on an Instron capillary rheometer with a capillary having an L/D of 33.1. Rabinowitsch corrections were applied to the data.

The normal stress data were obtained on the Instron Model 3250 rotary rheometer at 190°C using a 4-cm disc and a cone angle of 40 milliradians. The load cells were calibrated with a NBS Class-C weight.

The first normal stress difference N_1 was calculated from

$$N_1 = \frac{2F_z}{\pi R^2}$$

where F_z is the measured thrust normal to the disc and R is the radius of the disc.

MODEL

In an earlier publication,[6] the author interpreted the partitioning of molecular weights at any given shear rate $\dot{\gamma}$ (into those that contribute to the viscosity as they do at zero shear and those that do not) as the inability of molecular weights larger than the partitioning molecular weight M_c to fully relax in the time scale proportional to $1/\dot{\gamma}$. In order to apply the earlier model for application to elastic phenomena, we will make three assumptions. First, the onset on non-Newtonian behavior associated with a particular molecular species of molecular weight M implies that the maximum relaxation time associated with M is no longer operative. Second, the maximum allowed relaxation time τ_c is proportional to the reciprocal of the shear rate. Finally, we will assume that each molecule exhibits an almost continuous spectrum of relaxation times such that, in addition to its

characteristic longest relaxation time, a molecule of molecular weight M_k also undergoes the largest relaxations associated with molecular weights of M_{k-1}, M_{k-2}, etc., where $M_k > M_{k-1} > M_{k-2}$. This assumption is in apparent conflict with the theory of Rouse[10] in which the spacing between a molecule's longest relaxation time and its second longest is considerably larger than we have postulated.

These assumptions imply that at any given shear rate, both molecular weights and their characteristic relaxation times are partitioned into two classes: the relaxation times associated with the molecular weights are partitioned into those that are operative and those that are not, and the molecular weights into those whose maximum relaxation times are not operative and those whose maximum relaxation times are still operative. Further, there is a one-to-one relation between shear rate and the longest allowed relaxation time, τ_c.

Based upon the assumed partitioning of relaxation times as described above, the author proposes the following relation between the relaxation spectrum and the viscosity at any shear rate. The relation

$$\eta_0 = \int_0^\infty H d\tau \tag{1}$$

is obtained[11] from the general viscoelastic models for zero shear. *The present model implies that the only difference between a finite shear rate $\dot{\gamma}$ and zero shear is the cutting off of the relaxation times associated with molecular weights larger than that of the largest molecule undergoing Newtonian flow at $\dot{\gamma}$.* Consequently, zero-shear relations can be used at nonzero-shear rates using only the partition function (i.e., the relation between $\dot{\gamma}$ and τ_c) to describe the shear dependence. Consequently, eq. (1) then becomes

$$\eta(\tau_c) = \eta(\dot{\gamma}) = \int_0^{\tau_c} H d\tau \tag{2}$$

where the assumed relation between τ_c and $\dot{\gamma}$ is used.

For a monodisperse sample of molecular weight M greater than M_c, eq. (2) predicts that the viscosity will be solely a function of the maximum allowed relaxation time τ_c, which corresponds to the maximum allowed relaxation time for a molecule of molecular weight M_c. From the third assumption, it follows that all samples having $M > M_c$ should have viscosities equivalent to that of M_c. This is a good approximation[6] to the experimental behavior of narrow molecular weight distribution materials. In effect, a molecule's contribution to the viscosity is strictly dependent on the longest allowed relaxation time (allowed either by virtue of its molecular weight or the shear rate constraint).

Differentiating eq. (2) with respect to τ_c,

$$d\eta/d\tau_c = H(\tau_c) \tag{3}$$

The relation between the maximum allowed relaxation time and the largest molecular weight that acts in a Newtonian fashion, M_c, is[6] (based on the assumed proportionality between τ_c and $1/\dot{\gamma}$)

$$\tau_c = \alpha M_c^{3.33} \tag{4}$$

where α is a constant. The differentiation indicated in eq. (3) may now be performed (as shown in the Appendix) since η can be represented in terms of M_c[6]

(it should be noted that $\bar{M}_w{}^*$ and $\bar{M}_z{}^*$ in eq. 3 of ref. 6 are incorrect; their correct form is given in the Appendix):

$$H(\tau_c) = \frac{d\eta}{d\tau_c} = \frac{K}{3.33\alpha}\frac{(\bar{M}_w{}^*)^{2.36}\bar{A}_2}{(M_c)^{2.33}}\left\{3.36\left(\frac{\bar{M}_z{}^*}{\bar{M}_w{}^*}\right)^{0.51}\right.$$

$$\left. + 1.02\left(\frac{\bar{M}_z{}^*}{\bar{M}_w{}^*}\right)^{-0.49}\left[\frac{M_c - \bar{M}_z{}^*}{\bar{M}_w{}^*}\right]\right\} \quad (5)$$

where

$$\bar{M}_w{}^* = \sum_{i=1}^{C-1}\bar{h}_iM_i + M_c\sum_{i=C}^{\infty}\bar{h}_i$$

$$\bar{M}_z{}^* = \frac{\sum_{i=1}^{C-1}\bar{h}_iM_i{}^2 + M_c{}^2\sum_{i=C}^{\infty}\bar{h}_i}{\bar{M}_w{}^*}$$

$$\bar{A}_2 = \sum_{i=C}^{\infty}\bar{h}_i$$

and where $K = 10^{-12.296}$,[6] and h_i is the weight fraction of the ith component. The value for the exponent in the relation between relaxation time and M_c used here have been changed from that used in the earlier publication[6] on the basis of the availability of improved low shear rate data from the cone-and-plate viscometer and additional high molecular weight polystyrenes used in the calibration procedure.

The relation between the steady-shear elastic compliance and the relaxation spectrum has been shown to be

$$J_e{}^0 = \int_0^{\infty}\tau H d\tau/(\eta_0)^2 \quad (6a)$$

Analogous to the definition in eq. (2), the steady-shear elastic compliance at the shear rate $\dot{\gamma}$ is then taken as

$$J_e(\dot{\gamma}) = \int_0^{\tau_c}\tau H d\tau/[\eta(\dot{\gamma})]^2 \quad (6b)$$

or, substituting for $H(\tau'_c) = d\eta/d\tau'_c$,

$$J_e(\dot{\gamma}) = \int_0^{\tau_c}\tau'_c\frac{d\eta}{d\tau'_c}d\tau'_c/[\eta(\dot{\gamma})]^2 \quad (7)$$

Integrating the right side of eq. (7) by parts and substituting for τ_c and η,

$$J_e(\dot{\gamma}) =$$

$$\frac{\alpha\left\{M_c{}^{3.33}(\bar{M}_w{}^*)^{3.36}\left(\frac{\bar{M}_z{}^*}{\bar{M}_w{}^*}\right)^{0.51} - \int_0^{M_c}(\bar{M}_w{}^*)^{3.36}\left(\frac{\bar{M}_z{}^*}{\bar{M}_w{}^*}\right)^{0.51}d(M_c{}^{3.33})\right\}}{K(\bar{M}_w{}^*)^{6.72}\left(\frac{\bar{M}_z{}^*}{\bar{M}_w{}^*}\right)^{1.02}}$$

$$(8)$$

where

$$M_c = 540,000 \; \dot{\gamma}^{-0.300} \tag{9}$$

as determined empirically.[6]

Before applying the above relations, I should like to comment on a pertinent point made by the referee. It has been pointed out to me that it should be possible to predict $H(\tau,\dot{\gamma})$ from the viscosity (as predicted earlier[6]) and the relations as given by Shida and Schroff.[5] While this may in principle be possible, the shear dependence of the relations of Shida and Shroff is based on Graessley's model. Their derived shear dependence of the relaxation spectrum is not as postulated in my model (i.e., a sharp cutoff of the spectrum as a result of increasing shear rate), but rather a more complicated relation. Furthermore, as pointed out earlier,[6] one of the basic assumptions upon which my prediction of viscosity from the MWD is based is that a given molecule's contribution to the viscosity is independent of communal properties (in sharp contrast to the assumptions of Graessley's theory[4]). Because of these apparent disagreements, I feel that the relations formulated here are more consistent with the assumptions used earlier[6] to predict the steady-shear melt viscosity.

RESULTS AND DISCUSSION

First Normal Stress Difference

From eqs. (5) and (8) for the relaxation spectrum and steady-shear elastic compliance, respectively, it can be seen that there is only one unknown parameter, α, which is just the proportionality constant between the longest relaxation time for a molecule of molecular weight M, τ_m, and $M^{3.33}$. This parameter will be determined by comparing the experimentally determined first normal stress difference, N_1, to that predicted by the relation[11]

$$N_1 = 2J_e(\dot{\gamma})\sigma^2 \tag{10}$$

where $J_e(\dot{\gamma})$ is the shear rate-dependent elastic compliance as given in eq. (8), and σ is the shear stress.

The molecular weight distributions of the two samples employed to illustrate the use of the model are given in Table I. Sample A has a relatively broad MWD, while the MWD of B is considerably narrower. $J_e(\dot{\gamma})/\alpha$ was calculated from eq. (8) at various shear rates from the molecular weight distribution by approximating the integral by a modified Simpson's method.[12] The calculated values of $J_e(\dot{\gamma})/\alpha$ and $\eta(\dot{\gamma})$ were then used to calculate N_1/α from eq. (8) and the relation $\sigma = \eta\dot{\gamma}$, where η was calculated at the shear rate $\dot{\gamma}$, in the same manner as given in the previous publication.[6] By finding the multiplicative factor applied to $2J_e(\dot{\gamma})\sigma^2/\alpha$ that would produce coincidence with the experimental normal stress data, α was found to be equal to 1.4×10^{-19} from this procedure. The experi-

TABLE I
Molecular Weight Distributions of Samples A and B

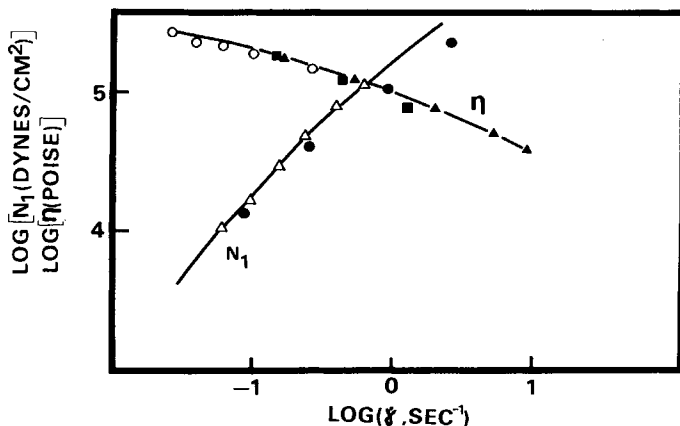| Sample	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_{z+1}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_z\overline{M}_{z+1}/\overline{M}_w{}^2$
A	12.1	158	732	1340	13.1	39
B	28.2	148	559	1261	5.2	32

Fig. 1. Variation of steady-shear melt viscosity η and first normal stress difference N_1 with shear rate for sample A. Curves are those predicted from the molecular weight distribution. Closed squares and triangles are experimental cone-and-plate and capillary viscosity data, respectively, and circles are experimental normal stress data from Instron. Open circles and triangles are cone-and-plate data supplied by Prof. W. W. Graessley.
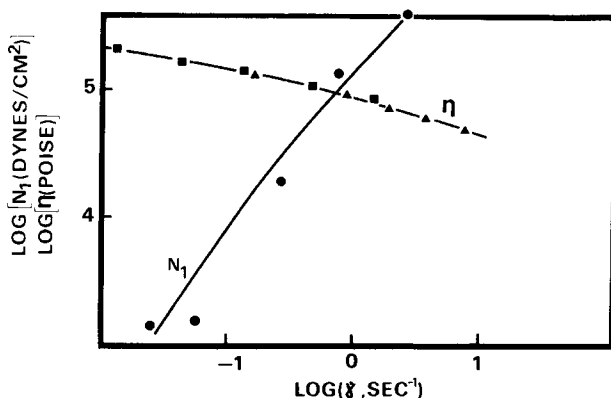

Fig. 2. Variation of steady-shear melt viscosity η and first normal stress difference N_1 with shear rate for sample B. Curves are those predicted from the molecular weight distribution. Squares and triangles are experimental cone-and-plate and capillary viscosity data, respectively, and circles are experimental normal stress data.

mental and predicted first normal stress difference and steady-shear viscosity data for samples A and B are given in Figures 1 and 2. The predicted shear rate dependence of the first normal stress and the steady-shear viscosity are in reasonable agreement with the experimental data over the limited shear rate range covered by the cone-and-plate viscometer. Both the positions and shapes of the curves for both samples, having quite different molecular weight distributions, are described by adjusting the one empirical parameter α.

Substituting 1.4×10^{-19} for α into eq. (4) and combining with eq. (9), we get

$$\tau_c = 1.7/\dot{\gamma} \tag{11}$$

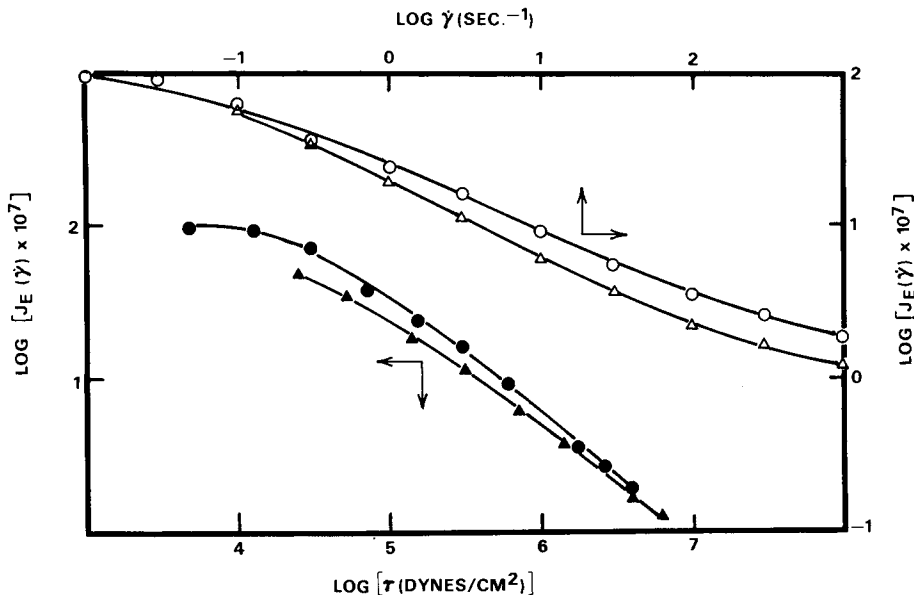Thus, the proportionality constant in the assumed proportionality of τ_c to $1/\dot{\gamma}$ is determined.

Fig. 3. Plot of the predicted dependence of steady-shear elastic compliance $J_e(\dot\gamma)$ on shear rate (open points) and shear stress (solid points). Sample A is represented by circles and sample B, by triangles.

Figure 3 is a plot of the predicted steady-shear elastic compliance as a function of shear rate. As can be seen in the figure, $J_e(\dot\gamma)$ is a monotonically decreasing function of shear rate producing a sigmoidal-shaped curve, which appears to approach a constant value at higher shear rates. This predicted decrease of $J_e(\dot\gamma)$ with $\dot\gamma$ is experimentally observed in a number of materials.[13] Graessley and Segal[14] have also experimentally observed a decrease in $J_e(\dot\gamma)$ with $\dot\gamma$ in concentrated solutions of broad molecular weight distribution polystyrene samples. However, since the agreement between the experimental and the predicted changes in normal stress with shear rate in Figures 1 and 2 is over a more limited shear rate range, the higher shear rate portions of the J_e curves represented in Figure 3 cannot be verified except by qualitative comparison to results on other systems.

The Relaxation Spectrum

The relaxation spectrum ought to be predictable from the MWD through eq. (5). I have chosen to compare the predicted $H(\tau)$ spectrum of a high-density polyethylene sample studied by Shida and Shroff (HD-173) from the molecular weight distribution as determined in our laboratory and eq. (5) (Fig. 4). The relaxation spectrum of Shida and Shroff was determined at low shear rates (8.0 $\times 10^{-3}$ sec^{-1}, where it is very nearly equivalent to the relaxation spectrum at zero shear rate). The molecular weight averages corresponding to the predicted relaxation times are also given. The predicted relaxation spectrum has been extended to very short relaxation times (high shear rates) for the purpose of illustrating the predictions of the model, even though experimentally unstable flow occurs under shear. The predicted relaxation spectrum compares favorably with
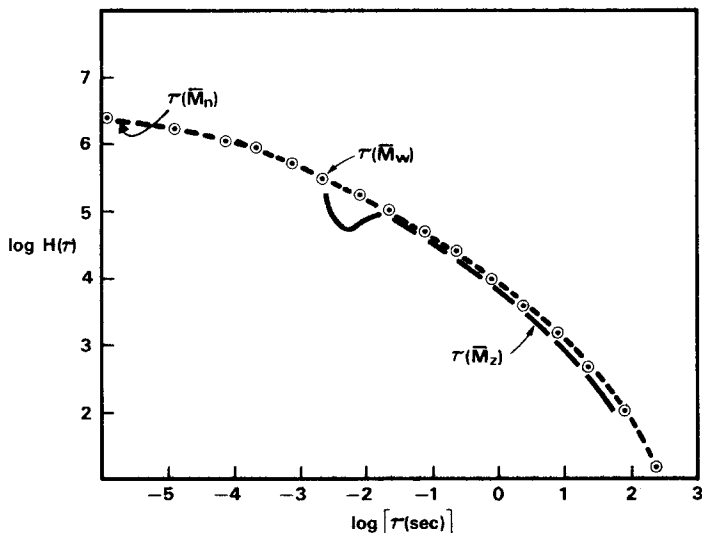
Fig. 4. Comparison of the relaxation spectrum as experimentally determined by Shida and Shroff[5] and that calculated from the measured molecular weight distribution. The calculated relaxation times corresponding to the various molecular weight averages are shown. Long-dashed line represents the data of Shida and Shroff. Points connected by short-dashed line are calculated relaxation spectrum at zero shear rate. The predicted relaxation spectrum has been extended to very short relaxation times for the purpose of illustrating the predictions of the model, even though experimentally unstable flow would be occurring at shear rates equivalent to these very short relaxation times.

the data of Shida and Shroff at the long relaxation end. At shorter relaxation times, however, the experimental relaxation spectrum shows both a maximum and a minimum, the reason for which is not clear. However, Shroff has shown[15] that the minimum-maximum at the shorter relaxation times can be removed by a change in the procedure of the calculation of $H(\tau)$ from experimental measurements. Consequently, the apparent deviation of the predicted and experimentally calculated relaxation spectra at the shorter relaxation times may be understandable.

The present model appears to be similar to the concept of Shida and Shroff[5] for relating the experimental relaxation spectrum to the steady-shear viscosity in that the effect of shear rate is such that the longer relaxations are progressively cut off. However, their treatment indicates that the effect of increasing shear rate is not to sharply cut off the long relaxations as indicated in the present model. Further, they state that the net effect of increases in shear rate on the melt viscosity is essentially the removal of the highest molecular weight molecules. In the "partition" model, however, the long relaxations associated with high molecular weight molecules are progressively not allowed, as the shear rate is increased, but the shorter relaxations associated with these high molecular weight molecules are still allowed and contribute to the steady-shear melt viscosity.

CONCLUSIONS

The partitioning of both molecular weights and their corresponding maximum relaxation times into the two classes appears justified in view of the good

agreement (over an admittedly limited shear rate range) between the experimental results on both steady-shear viscosity and normal stress data and those predicted from the molecular weight distribution. The fact that no specific mechanism describing the molecular relaxations and nature of entanglement coupling is given can be considered both a source of strength and weakness of the presented model. The "partition" model has been shown to provide a simple connection between molecular weight, relaxation time, and shear rate, which should prove useful in the relation of molecular structure to observed elastic phenomena such as parison swell and melt instability at high shear rates. Further, the concept upon which the model presented here is predicated (i.e., a molecules contribution to both the melt viscosity and elastic properties is simply a function of the largest allowed relaxation time) should provide the basis for a more thorough and elegant theoretical treatment.

The model presented is quite useful in that both the viscosity and elastic parameters can be easily and routinely calculated from the molecular weight distribution data by anyone having access to a small computer. In view of the success of the model for high-density polyethylene melts, the applicability to other polymer systems should be investigated. We are presently involved in the application to polystyrene melts.

Appendix

From the chain rule

$$\frac{d\eta}{d\tau_c} = \frac{d\eta}{dM_c}\frac{dM_c}{d\tau_c} \tag{12}$$

where

$$\frac{dM_c}{d\tau_c} = \frac{1}{3.33\alpha M_c{}^{2.33}}$$

But as shown in reference 6, the viscosity at any nonzero shear rate may be represented as

$$\eta(\dot{\gamma}) = K(\bar{M}_w{}^*)^{3.36}\left(\frac{\bar{M}_z{}^*}{\bar{M}_w{}^*}\right)^{0.51} \tag{13}$$

where

$$\bar{M}_w{}^* = \int_0^{M_c} M\frac{da}{dM}dM + M_c\int_{M_c}^{\infty}\frac{da}{dM}dM \tag{14a}$$

$$\bar{M}_z{}^* = \frac{\int_0^{M_c} M^2\frac{da}{dM}dM + M_c{}^2\int_{M_c}^{\infty}\frac{da}{dM}dM}{\bar{M}_w{}^*} \tag{15a}$$

and a is the cumulative distribution function.[16] Equations (14a) and (15a) can also be written in terms of summations as

$$\bar{M}_w{}^* = \sum_{i=1}^{c-1} \bar{h}_i M_i + M_c\sum_{i=c}^{\infty}\bar{h}_i \tag{14b}$$

and

$$\bar{M}_z{}^* = \frac{\sum_{i=1}^{c-1}\bar{h}_i M_i{}^2 + M_c{}^2\sum_{i=c}^{\infty}\bar{h}_i}{\bar{M}_w{}^*} \tag{15b}$$

where $\bar{h}_i$ is the weight fraction of the ith homolog of molecular weight M_i.

As a result, it can be shown that

$$\frac{dM_w{}^*}{dM_c} = \int_{M_c}^{\infty} \frac{da}{dM}\, dM \equiv \bar{A}_2 \qquad (16)$$

and

$$\frac{d(\bar{M}_z{}^*/\bar{M}_w{}^*)}{dM_c} = \frac{2(\bar{A}_2 M_c - \bar{A}_2 \bar{M}_z{}^*)}{(\bar{M}_w{}^*)^2} \qquad (17)$$

Finally, to arrive at eq. (16) of the text, the definitions of $\bar{A}_2$, $\bar{M}_w{}^*$, and $\bar{M}_z{}^*$ are put in summation form for easy calculation from gel permeation-chromatographic data.

References

1. W. W. Graessley, *Advances in Polymer Science,* Vol. 16, Springer-Verlag, New York, 1974.
2. W. W. Graessley, *J. Chem. Phys.,* **43,** 2696 (1965).
3. W. W. Graessley, *J. Chem. Phys.,* **47,** 1942 (1967).
4. W. W. Graessley, *J. Chem. Phys.,* **54,** 5143 (1971).
5. M. Shida and R. N. Shroff, *Trans. Soc. Rheol.,* **14,** 605 (1970).
6. B. H. Bersted, *J. Appl. Polym. Sci.,* **19,** 2167 (1975).
7. J. A. Faucher, *J. Appl. Phys.,* **32,** 2336 (1961).
8. G. Ajroldi, C. Garbuglio, and G. Pezzin, *J. Polym. Sci.,* **5,** 289 (1967).
9. S. I. Abdel-Khalik, Ole Hassager, and R. Byron Bird, *Polym. Eng. Sci.,* **14,** 859 (1974).
10. P. E. Rouse, *J. Chem. Phys.,* **21,** 1272 (1953).
11. J. D. Ferry, *Viscoelastic Properties of Polymers,* Wiley, New York, 1961, 29.
12. J. Olmsted, *Real Variables,* Appleton-Century-Crofts, New York, 1959, 146.
13. T. W. Spriggs, J. D. Huppler, and R. B. Bird, *Trans. Soc. Rheol.,* **10,** 191 (1966).
14. W. W. Graessley and L. Segal, *Macromolecules,* **2,** 47 (1969).
15. R. N. Shroff, *J. Appl. Phys.,* **41,** 3652 (1970).
16. H. Pickett, M. Cantow, and J. Johnson, Third International Gel Permeation Chromatography Seminar, Geneva, Switzerland, 1966.