

## Poly(ethylene sulfide). IV. A Rheological Method for Determination of "Apparent Molecular Weight"

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### Synopsis

By combining a number of theoretical relationships concerning the effect of molecular weight on melt rheology, an equation may be derived for conversion of melt indexer flow rate to "apparent molecular weight." In spite of certain evident theoretical shortcomings of this derivation, the method was applied to the determination of the molecular weight of highly crystalline insoluble poly(ethylene sulfide), for which no other method appeared to be satisfactory. When applied to polymer specimens of presumably known molecular weight (e.g., certain ionically initiated specimens), reasonable agreement was found.

### INTRODUCTION

Studies have been reported from this and several other laboratories<sup>1-12</sup> on poly(ethylene sulfide), a highly solvent resistant thermoplastic resin. Although several unconventional high-temperature solvents were known for this polymer, routine use of solution viscometry for relative molecular weight determination seemed to be overly difficult and undesirable, particularly since the flow times of unstabilized solutions in all solvents fell rapidly<sup>1,3</sup> and we were unable to discover useful solution stabilizers. Melt viscometry was a more adaptable procedure, particularly after development of suitable melt-flow stabilizers.<sup>13</sup> There remained the problem of absolute molecular weight measurements, to provide at least order-of-magnitude assurance that the desired high molecular weight polymer had been prepared.<sup>14</sup> Even in the absence of colligative property calibration, intrinsic viscosity values may usually be relied on for this purpose. It is a useful rule-of-thumb, for instance, that molecular weight is of the order of  $10^5$   $[\eta]$ , but no such simple rule was known for melt viscosities, particularly since the latter are extremely sensitive to both temperature and molecular weight. Some theoretical developments do give promise, however, that melt viscosity or amorphous-phase stress relaxation measurements can be used to give a measure of molecular weight which need be only indirectly calibrated by solution property measurements.

The key observation in the development of a direct molecular weight-melt viscosity relationship was Tobolsky and Murakami's finding that,<sup>15</sup> for several polymers, the same "universal" relationship holds between the

maximum relaxation time (a rheological property) at the glass transition temperature  $T_g$  and the molecular size as measured under "theta conditions." Since this finding included the already known "universal" expression for the temperature dependence of rheological time factors above  $T_g$ ,<sup>16</sup> while molecular size may be readily converted to molecular weight, it seemed useful to deduce a melt viscosity-molecular weight relationship and investigate its applicability to poly(ethylene sulfide).

### FORMULATION OF THE KNOWN EXPRESSIONS

According to Tobolsky and Murakami, for polyisobutylene, polystyrene, and poly(vinyl acetate),

$$\log \tau_m \text{ (seconds)} = -2.21 - \mathfrak{F}(T, T_g) + 6.8 \log (\bar{r}_\theta / l_0) \quad (1)$$

where  $\tau_m$  = relaxation time,  $\bar{r}_\theta$  = root-mean-square end-to-end distance under theta conditions (e.g., in a solvent at the point of precipitation),  $l_0$  = length of the carbon-carbon bond, 1.54 Å,

$$\mathfrak{F}(T, T_g) = 17.44 (T - T_g) / (51.6 + T - T_g), \quad (2)$$

the shift factor in the Williams-Landel-Ferry equation,<sup>16</sup>  $T$  = temperature at which  $\tau_m$  is measured, and  $T_g$  = glass transition temperature of polymer.

As a first step in utilizing eq. (1), we assumed that this relationship holds for linear polymers with bonds other than C-C in the main chain. In other words, all local chain stiffness effects are expressed in the value of  $\bar{r}_\theta$  for a given polymer. (The numerical value of the term  $-6.8 \log l_0$  may be incorporated into the universal constant of the equation.)

For conversion from root-mean-square chain dimensions to molecular weight,  $M$ , we used the Fox-Flory expression<sup>17</sup>:

$$K = \Phi(\bar{r}_\theta^2 / M)^{3/2} \quad (3)$$

where  $\Phi$  is a universal constant and  $K$  is a chain stiffness parameter which is experimentally defined by

$$[\eta]_\theta = KM^{1/2} \quad (4)$$

where  $[\eta]_\theta$  is the intrinsic viscosity under theta conditions.

It should also be explicitly pointed out that the use of eq. (2) to define  $\mathfrak{F}(T, T_g)$  at temperatures far above  $T_g$  is at best a dubious extrapolation; it would be preferable to establish the exact form of the temperature dependence experimentally when this becomes possible.

Finally, an experimental technique for measuring  $\tau_m$  had to be selected. Tobolsky and Murakami used stress relaxation<sup>15,18</sup>; in principle, at least, zero-shear melt viscosity  $\eta_m$  is equally valid. The relationship between viscosity and  $\tau_m$  for monodisperse polymers in dilute solution has been de-

veloped by several workers<sup>19-22</sup>; we used the theory of Rouse<sup>19</sup> as extended to undiluted polymers by Ferry et al.,<sup>23</sup> namely,

$$\tau_m = \frac{6\eta_m M}{\pi^2 \rho RT} \quad (5)$$

where  $\rho$  = polymer melt density and  $R$  = the gas constant.

Equations (1) and (5) are established only for polymers which are either monodisperse or of a specific form of molecular weight distribution (MWD), whereas eqs. (3) and (4) apply to theta-viscosity average molecular weights and eq. (2) is substantially independent of MWD. We shall beg the question of what molecular weight average will be obtained from combination of these relationships, pointing out only that direct calibrations of more tractable polymers have usually been related to  $\bar{M}_w$ , the weight-average molecular weight.<sup>24,25</sup>

The indirect solution property calibration referred to previously is required to determine the constant  $K$  in eq. (3). In the absence of any relevant experimental data,  $K$  may be taken as  $10^{-3}$ , which is the order of magnitude it usually has. If  $K$  is experimentally known for a reasonably analogous or homologous polymer, this value will usually be more suitable, after making obvious geometric corrections. For poly(ethylene sulfide), it should be possible to adapt  $K$  determined on poly(propylene sulfide), or on soluble copolymers of ethylene and propylene sulfides, when such data become available.

### ALGEBRAIC COMBINATION OF KNOWN EQUATIONS

The generalized form of eq. (1) is

$$\log \tau_m = -3.485 - \mathfrak{F}(T, T_\theta) + 6.8 \log \bar{r}_\theta \quad (6)$$

with  $\tau_m$  in seconds and  $\bar{r}_\theta$  in Å. From eq. (5),

$$\log \tau_m = \log \left( \frac{\eta_m / \rho}{T} \right) + \log M - \log (\pi^2 R / 6) \quad (7)$$

with  $\tau_m$  in seconds,  $\eta_m / \rho$  in stokes, and  $R$  in ergs/mole-°C. Consequently

$$3.4 \log \bar{r}_\theta^2 - \log M = 3.485 + \mathfrak{F}(T, T_\theta) + \log \left( \frac{\eta_m / \rho}{T} \right) - \log (\pi^2 R / 6). \quad (8)$$

Substituting from eq. (3), where  $\bar{r}_\theta$  is in cm, and inserting  $R = 8.3144 \times 10^7$ ,

$$3.4 \log M(K/\Phi)^{2/3} - \log M = \log \left( \frac{\eta_m / \rho}{T} \right) + \mathfrak{F}(T, T_\theta) - 59.05. \quad (9)$$

The proper value to choose for  $\Phi$  is somewhat controversial; we followed Krigbaum<sup>26</sup> in setting  $\Phi = 2.4 \times 10^{21}$ , so that

$$2.4 \log M + 3.4 \log K^{2/3} = \log \left( \frac{\eta_m/\rho}{T} \right) + \mathfrak{F}(T, T_g) - 10.59 \quad (10)$$

or

$$\log MK^{17/18} = \frac{1}{2.4} \log \left( \frac{\eta_m/\rho}{T} \right) + \frac{1}{2.4} \mathfrak{F}(T, T_g) - 4.41. \quad (11)$$

The quantity  $MK^{17/18}$  will be of the order of  $10^{-3}M$  and can serve as a rough measure of the molecular weight when  $K$  is unknown, just as  $[\eta]$  serves for readily soluble polymers.

It is evident from eq. (10) that the melt viscosity will be proportional to the 2.4 power of the molecular weight. Most direct calibrations of this relationship with other polymers have taken the form<sup>24,25</sup>

$$\eta_m = (\text{const})M^{3.4} \quad (12)$$

and this exponent has been theoretically justified by Bueche.<sup>27</sup> Lower values of the exponent have been reported for nonzero-shear melt viscosities, in many cases.<sup>28</sup> Since the melt indexer is a nonzero-shear instrument, the lower value of the exponent may be acceptable. In any case, empirical justification was eventually resorted to and will be described in a subsequent section.

## APPLICATION TO POLY(ETHYLENE SULFIDE)

### Measurement of $\eta_m$

There are several likely sources of error<sup>29-34</sup> in using the standard melt indexer<sup>35</sup> to determine  $\eta_m$ . Such errors are of far less significance, however, than the change in melt viscosity of poly(ethylene sulfide) due to thermal degradation at the test temperature. Hence, for our purposes, it sufficed to calculate  $\eta_m$  from the flow rate, pressure applied, and measured dimensions of the melt indexer, by the expression

$$\eta_m = \frac{p\pi r^4 \rho}{8Ql} \quad (13)$$

where  $p$  = applied pressure, dynes/cm<sup>2</sup>;  $r$  = orifice radius, cm;  $Q$  = flow rate, gm/sec; and  $l$  = orifice length, cm;  $\eta_m$  will then be given in poises, and  $\eta_m/\rho$  in stokes.

Equations (10) and (11) utilize the kinematic melt viscosity, which is directly calculable from eq. (13). Hence, the polymer melt density need not be known for this purpose.

### Estimation of $T_g$

For poly(propylene sulfide),  $T_g$  had been found to be  $-25^\circ\text{C}$ ,<sup>36</sup> while a 50%<sub>m</sub> copolymer of ethylene sulfide-propylene sulfide had  $T_g = -40^\circ\text{C}$ .<sup>36</sup> Simple linear extrapolation gave  $T_g$  of poly(ethylene sulfide) with sufficient

accuracy for our present purpose. Taking  $T_g = -55^\circ\text{C}$  ( $218^\circ\text{K}$ ), the quantity  $\mathfrak{F}(T, T_g)$  was calculated from eq. (2). Published data show  $T_g$  of poly(propylene sulfide) to be  $-52^\circ\text{C}$ .<sup>39</sup> Simple linear extrapolation would then predict a higher value for  $T_g$  of poly(ethylene sulfide); indeed, it may even approach room temperature.<sup>3</sup> This will decrease  $\mathfrak{F}(T, T_g)$  somewhat.

### Development of Working Equations

By use of certain melt-stabilizing systems,<sup>13</sup> melt flow rate could be measured in the melt indexer with little apparent degradation, even at temperatures as high as  $235^\circ\text{C}$ . From the known dimensions of the melt indexer and the known load used, the kinematic viscosity could be related to the melt flow rate by

$$\eta_m/\rho = 1.055 \times 10^4/G \quad (14)$$

where  $G$  = melt flow rate, g/min, and  $\eta_m/\rho$  = kinematic viscosity, stokes; flow through orifice: 0.0825 in. diam  $\times$  0.315 in. length; load: 2160 g on 0.375 in. diam piston.

By substitution of eq. (14) into eq. (11), taking  $K = 10^{-3}$ , we obtain

$$\log M = 0.10 - (1/2.4) [\log (GT) - \mathfrak{F}(T, T_g)]. \quad (15)$$

At  $235^\circ\text{C}$ ,

$$\log M = 5.14 - 0.4167 \log G. \quad (16)$$

At  $215^\circ\text{C}$ ,

$$\log M = 5.08 - 0.4167 \log G. \quad (17)$$

Since, even with stabilized melts, the flow rate is not perfectly constant, we adopted the procedure of weighing the amount extruded in each minute after unblocking the melt indexer orifice, plotting the logarithm of these cut weights against the time at which the cut was taken, and extrapolating to the time of unblocking the orifice, to obtain  $G$ .

### Comparison With Polymers of Known Molecular Weight

Most of the poly(ethylene sulfide) polymers we have dealt with were prepared using a heterogeneous diethylzinc-water catalyst, frequently using the "seed polymer" technique.<sup>1</sup> Consequently no ideal molecular weight could be inferred from catalyst concentration. In later work, some polymers were prepared using a soluble anionic catalyst.<sup>37</sup> In Figure 1 is shown a comparison of  $\bar{M}_n$  (calculated from the ratio of monomer used to catalyst) with apparent molecular weight obtained by eq. (16) from melt indexer flow rate of stabilized polymer at  $235^\circ\text{C}$ . Note in particular the series of data obtained at a monomer:catalyst ratio of 10,000:1, stopped at various conversions. This was taken to indicate that these polymers were suitable for calibration purposes, and a number of others were prepared, at various monomer:catalyst ratios. Also included in Figure 1 are data obtained with

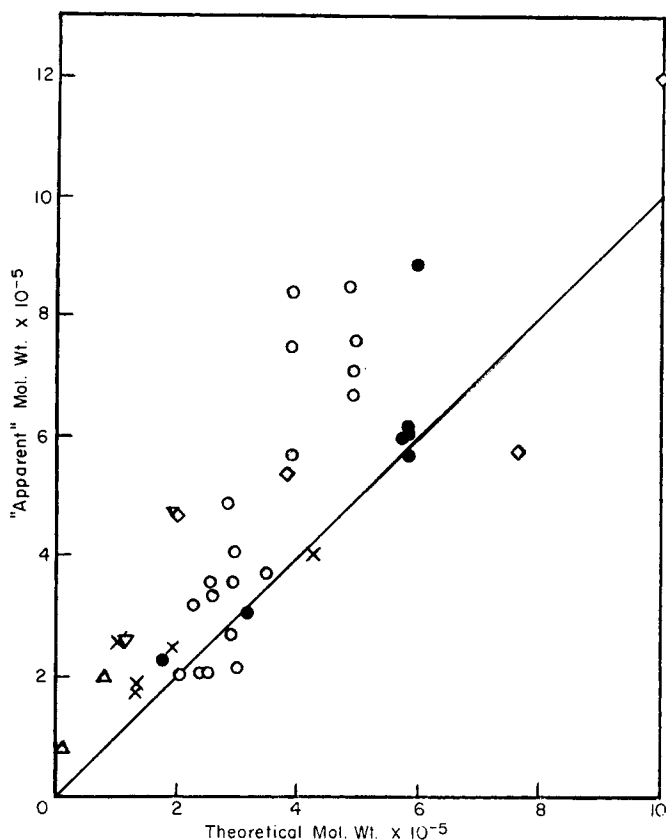


Fig. 1. Comparison of apparent molecular weight from melt flow viscosity using eqs. (15), (16), or (17), with theoretical number-average molecular weight calculated from monomer:catalyst ratio: (●) polymers prepared using soluble anionic catalyst at monomer:catalyst ratio of 10,000:1, stopped at various conversions; (○) other polymers prepared using this catalyst, at various ratios; (×) polymers prepared using other soluble anionic catalysts; (▽) polymers prepared in this laboratory using DABCO initiator; (◇) polymers prepared and tested elsewhere<sup>38</sup> using DABCO initiator; (△) polymers reported by Nicco et al.<sup>3</sup> using potassium *tert*-butoxide initiator.

some other soluble anionic catalysts<sup>37</sup> as well as with triethylenediamine (DABCO),<sup>37,38</sup> assumed to act as a monofunctional initiator. Two data points using potassium *tert*-butoxide were taken from a recent publication<sup>3</sup>; it was necessary to assume a melt density (1.3 was chosen, but a more probable value of 1.15–1.2 would not shift the points significantly) and apply the temperature correction terms of eq. (15).

It appears from Figure 1 that these apparent molecular weights are the order-of-magnitude approximations which we set out to obtain. Scatter in the data is too great to permit true calibration, however. When these data are plotted logarithmically as kinematic melt viscosity versus calculated  $\bar{M}_n$ , virtually any slope from 2.0 to 3.5 appears to fit, with rather poor

correlation coefficients of 0.80 to 0.85. In particular, if the triethylenediamine-initiated and potassium *tert*-butoxide-initiated data are rejected, a least-squares fit to the remaining data has a slope of 2.165 with a correlation coefficient of 0.84.

## CONCLUSIONS

An equation has been derived which, for poly(ethylene sulfide), permits direct conversion of melt indexer flow rate to "apparent molecular weight." The weakest link in the chain of derivation is in converting melt indexer apparent melt viscosity to maximum viscoelastic relaxation time. This results in a logarithmic melt viscosity-molecular weight relationship which differs significantly from that generally accepted for most polymers (exponent is 2.4 rather than 3.4). Attempted verification of the equation by measuring melt flow of certain anionically initiated poly(ethylene sulfide) polymers indicated qualitative agreement, but the absolute values of "apparent molecular weight" are in some doubt. Because of the exponent problem, even relative values may be in error. A compensating factor may be that the melt indexer apparent melt viscosity is certainly not a zero-shear melt viscosity, and exponents lower than 3.4 are known to be appropriate at shear rates greater than zero.

Other sources of absolute error include: various non-Newtonian corrections to apparent melt viscosity; mechanical problems in measuring true flow rate and true melt temperature; possible melt fracture, plug-flow, and turbulence effects in the melt indexer; the applicability of the relationship used between maximum relaxation time and molecular weight; the applicability of the temperature-melt viscosity relationship used and the need to specify  $T_g$  with this relationship; the choice of a chain stiffness factor when solution properties cannot be measured; the validity of the Fox-Flory relation between molecular weight and chain extension in the melt; and, finally, the question of what kind of average molecular weight is theoretically related to melt viscosity.

In principle, the same relationship could be used for thioether copolymers, with appropriate correction of chain stiffness factor and  $T_g$ , if needed.

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