Determination of Polymer Crystal Molecular Weight Distribution by DSC

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ABSTRACT

The Flory equation provides a tool to relate the melting temperature of a polymer to the molecular weight of its crystals. The equation uses the melting temperature and heat of fusion of 100% crystalline polymer, along with the polymer melting temperature profile to achieve this result. Values for the 100% crystalline polymer melting temperature and heat of fusion may be estimated from low molecular weight oligomers or, alternatively, from the ATHAS database. Application of the Flory equation on a point-by-point basis to a DSC melting profile yields crystal molecular weight distribution from which average molecular weight values are obtained. Such profiles provide a qualitative visual representation of the effects of thermal treatment on a polymer.

INTRODUCTION

Most thermal analysts intuitively know that the melting temperature of a polymer and the width of the melting endotherm are related to its molecular weight and molecular weight distribution. Rarely, however, is quantitative molecular weight and distribution information derived from the DSC melting profile.

The Flory equation (*1),* well known to the polymer chemist but rarely used by the thermal analyst, provides a tool to calculate polymer crystal molecular weight and molecular weight distribution from DSC melting curves. The relationship between polymer molecular weight (*MW*, in g mol^{-1}) and the melting temperature (*T*, in K) is given by:

$$MW = \frac{2\,R\,T\,Tmax}{H\,(Tmax - T)} \qquad \text{(eq. 1)}$$

where *R* is the molar gas constant (= 8.314 J g^{-1} mol^{-1}), *H* is the enthalpy of fusion for 100 % crystalline material (in J g^{-1}), and *Tmax* is the maximum melting temperature of the polymer archetype (in K).

To evaluate this equation, values for *H* and *Tmax* are required. The Flory equation itself may be used to obtain these values through the substitution of the molar enthalpy of melting ($\mathcal{H}$) and the degree of polymerization (*DP*) into equation 1. *DP* is the polymer molecular weight divided by the molecular weight of the repeat unit.

$$\mathcal{H} = \frac{2\,R\,T\,Tmax}{DP\,(Tmax - T)} \qquad \text{(eq. 2)}$$

Equation 2 has the form of $Y = mX + b$ where a plot of $\mathcal{H}$ for individual low molecular weight oligomers versus the reciprocal of the degree of polymerization yields an intercept, the value for which represents H for the 100 % crystalline polymer.

Another form of the Flory equation is shown in Equation 3. Here the melting temperatures for a series of low molecular weight oligomers may be plotted as a function of $1/DP$, yielding a line with an intercept, the value for which is $1/Tmax$.

$$\frac{1}{T} = \frac{2\,R}{H\,DP} + \frac{1}{Tmax} \qquad \text{(eq. 3)}$$

As an example, Figure 1 shows the molar heat of fusion for even linear normal alkanes ranging from n-butane through n-dotriacontane plotted as a function of reciprocal degree of polymerization. These values were obtained from the literature (*2*) and represent low molecular weight oligomers for polyethylene. A straight line results so that the value for H is easily obtained at the intercept.
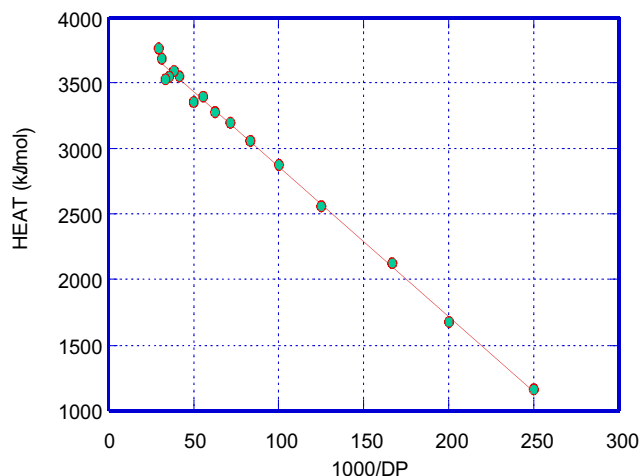

Fig. 1 Even Linear Alkane Heat of Fusion

Similarly, a plot of reciprocal melting temperature for this same alkane series versus reciprocal degree of polymerization is shown in Figure 2. The curve is less linear than with the heat of fusion but is easily fit with a second order polynomial to obtain the intercept of 1/ *Tmax*.
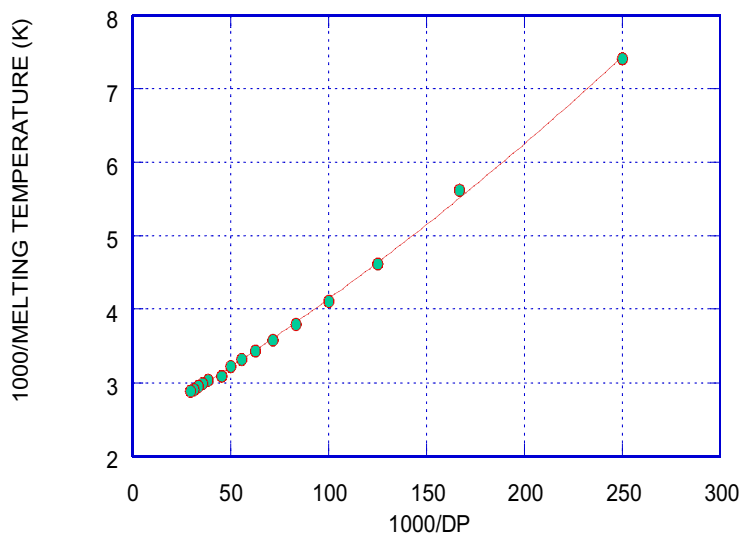
Fig. 2 - Even Alkane Melting Temperature

This process, while convenient for polyolefines, where the normal hydrocarbons represent low molecular weight oligomers, is difficult for most polymers due to the scarcity of oligomers. Fortunately Wunderlich and co-workers at the University of Tennessee have collected from the literature best estimates for the values for *H* and *Tmax* for a large number of polymers *(3).*

Once values for *H* and *Tmax* are obtained, they may be used to evaluate the original Flory Equation. To determine molecular weight distribution, one starts with the melting endotherm profile for the polymer of interest. The individual data points are normalized using the peak heat flow to produce a distribution. On a point-by-temperature-point basis, individual heat flow values are then submitted to equation 1 and the corresponding molecular weight distribution calculated. The usual processes may then be used to obtain the mode, number average, weight average and Z-average crystal molecular weight. Molecular weight distributions are usually plotted on a logarithmic basis.

Figure 3 shows the crystal molecular weight distribution measured by DSC, on the left, compared to that obtained by size exclusion chromatography for NIST SRM 1475A polyethylene, on the right. The figure shows that the mode (peak) molecular weight for the polymer crystals is a factor of 40 times smaller than that for the whole polymer. In addition, the molecular weight distribution itself is much narrower in the crystal case with the mode at 723 g/mol. For the 14 g/mol per repeat unit for polyethylene, this mode crystal size represents only about 50 repeat units, a surprisingly low value.

RESULTS AND DISCUSSION

Physical properties of polymers usually depend upon crystalline structure. For this reason, the crystal molecular weight and molecular weight distribution should be a powerful tool for observing performance differences resulting from
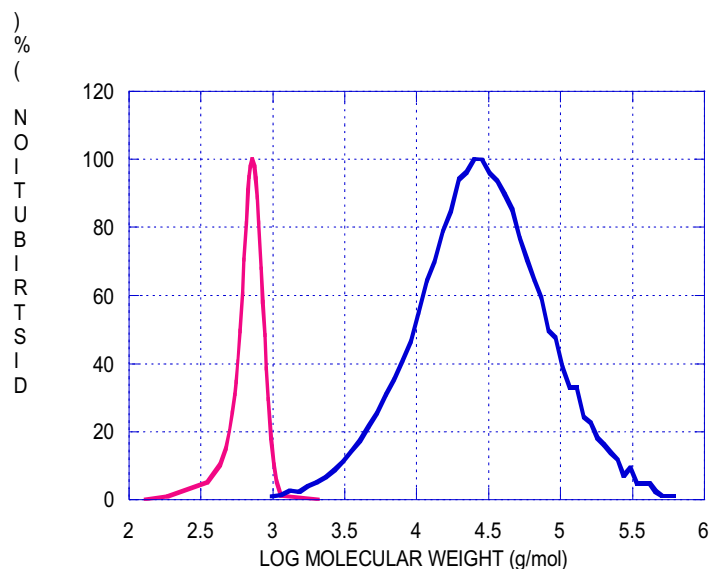
Fig. 3 - Comparative Molecular Weight Distributions

differing thermal histories. Examples examined indicate that most dramatic changes are observed in the extremes of the molecular weight distribution.

The effect of thermal history on crystal molecular weight is shown in Figure 4. Here the molecular weight distribution for a low molecular weight polyethylene on an "as received" basis is compared, on the left, with that for a sample cooled at 2 K min^{-1} on the right. For the fast crystallizing polyethylene, the slow cooling increases the mode molecular weight. This is not always the case. Figure 5 shows a similar comparison for ultra-high molecular weight polyethylene. Here the thermally treated material has a lower mode.

CONCLUSIONS

The Flory equation may be used to create crystal molecular weight distributions for polymers from the DSC derived melting endotherms. These results show that average crystal molecular weights are much different (and lower) than the size exclusion chromatography results. The determination of crystal molecular weight and distribution is helpful in visualizing the effects of thermal history on polymer structure.
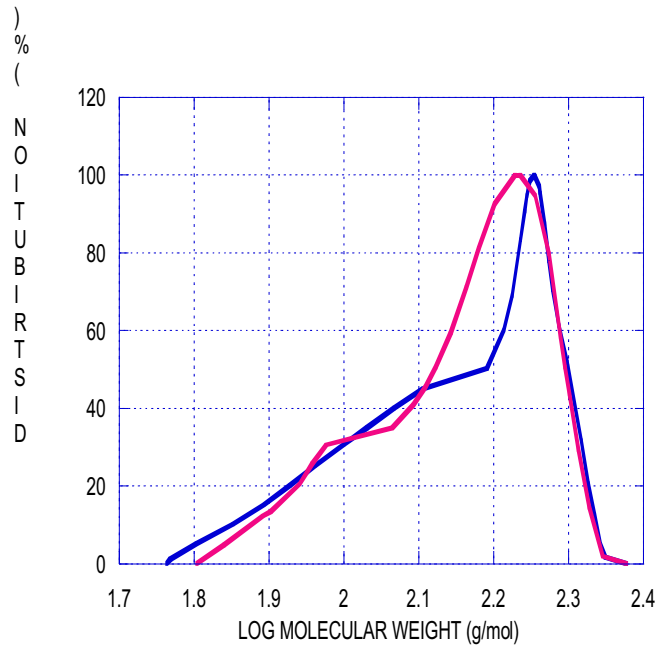
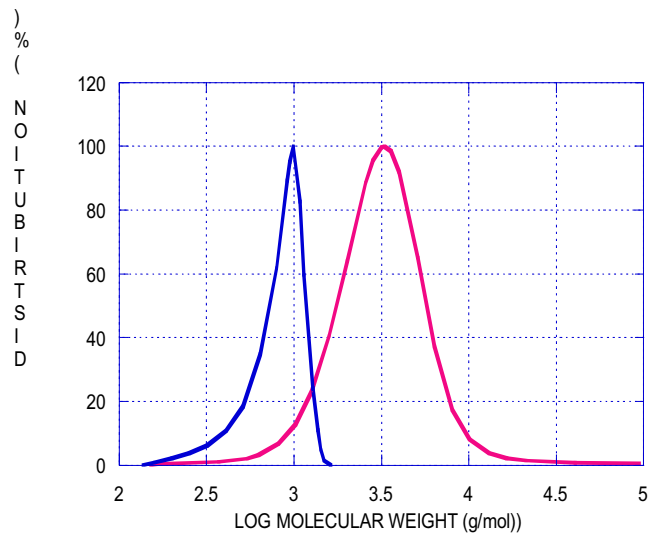Fig. 4 - Heat Treatment of a Low Molecular Weight Polyethylene

Fig. 5 - Heat Treatment of Ultra-High Molecular Weight Polyethylene

REFERENCES

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