

## ***Estimation of Molecular Weight Error for Concentration Uncertainties in the Intrinsic Viscosity Determination***

### **INTRODUCTION**

In the course of running certain large-scale polymerization reactions, it was necessary to determine when a specified molecular weight was attained. Intrinsic viscosity was selected for molecular weight measurement since the technique was rapid and experimentally simple. Although the polymer was prepared in solvent at a target value of concentration, the nature of the process led to significant random deviations resulting in a bulk solution concentration which was only approximately known. Since it was impractical to desolvate the sample while the reaction was in progress, the stock solution for intrinsic viscosity measurements was prepared by direct dilution of the bulk system. When the bulk concentration differed from the target value, this procedure introduced considerable uncertainty in intrinsic viscosity<sup>1</sup> and hence, in molecular weight. In this paper, a general equation is derived which expresses the error in calculated molecular weight as a function of the relative deviation of concentration from the target value and the power-law exponent of the Mark-Houwink<sup>2</sup> equation. The relation shows the error is smaller if the true bulk concentration is higher than the target value and if the polymer is in a good solvent rather than a poor one.

### **DISCUSSION**

In order to obtain a required minimum molecular weight and still take into account the possible intrinsic viscosity error (resulting from a given degree of uncertainty in the bulk concentration), the polymerization was carried out to a higher value of intrinsic viscosity (i.e., molecular weight) than actually required. Although a higher molecular weight could offset the error resulting from concentration uncertainties, it was desirable to keep the additional increment to a minimum since this resulted in large, undesirable increases in bulk viscosity. It was necessary, therefore, to calculate the minimum additional molecular weight increment which would just overcome the possible concentration-uncertainty error. In this way, although the bulk viscosity would be higher than the optimum value, it would be kept as close to the optimum as possible.

### **THEORETICAL ANALYSIS**

Intrinsic viscosity  $[\eta]$  can be obtained by measuring the specific viscosity  $\eta_{sp}$  of a series of dilutions of a stock solution.<sup>1</sup> These values are divided by their respective concentrations to determine reduced viscosity  $\eta_r$ , which is then plotted versus concentration  $C$  according to the Huggins equation<sup>3</sup>:

$$\eta_r = \frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C. \quad (1)$$

The intrinsic viscosity is obtained by extrapolating the resulting line to zero concentration.

If a stock solution of target concentration  $C_T$  is prepared from a bulk solution of *known* target concentration  $X_{BT}$ , the position of the resulting line on  $\eta_{sp}/C$ -versus- $C$  coordinates will be correct. However, if the bulk concentration  $X_B$  differs from the target value, the stock solution concentration  $C$  will not equal the assumed value  $C_T$  and the calculated values of reduced viscosity  $\eta_r$  will be in error. If  $C > C_T$ , this has the effect of shifting the Huggins line below and to the right of the true position (resulting in a lower calculated intrinsic viscosity). If  $C < C_T$ , the line will be shifted above and to the left (resulting in a higher calculated intrinsic viscosity). Thus, it is necessary to express

the calculated reduced viscosity as a function of the target  $X_{BT}$  and true bulk polymer concentration  $X_B$ .

The true concentration of the stock solution,  $C$ , in g/dl, can be expressed as

$$C = GX_B. \quad (2)$$

In this expression,  $G$  is the weight of bulk polymer solution diluted to 1 dl. The bulk polymer solution contains  $X_B$  grams polymer per gram of solution. If the bulk polymer concentration is *assumed* to be a target value  $X_{BT}$ , then eq. (2) is restricted to

$$C_T = GX_{BT} \quad (3)$$

where  $C_T$  is the target concentration of the stock solution. Since eqs. (2) and (3) must be true simultaneously,

$$C = \left( \frac{X_B}{X_{BT}} \right) C_T. \quad (4)$$

The calculated reduced viscosity  $\eta_r^*$  is defined as

$$\eta_r^* = \frac{\eta - \eta_0}{\eta_0 C} \quad (5)$$

where  $\eta$  and  $\eta_0$  are the stock solution and solvent viscosities, respectively. Substituting (4) into (5), we obtain

$$\eta_r^* = \left( \frac{\eta - \eta_0}{\eta_0 C_T} \right) \cdot \frac{X_{BT}}{X_B}. \quad (6)$$

If  $X_B = X_{BT}$ , the calculated reduced viscosity becomes the true reduced viscosity  $\eta_r$ . It can also be seen from eq. (6) that the calculated reduced viscosity  $\eta_r^*$  is the product of the reduced viscosity obtained by assuming the stock solution is of concentration  $C_T$  (defined as  $\eta_{rT}$ ) and the ratio of the target/true bulk polymer concentrations:

$$\eta_r^* = \eta_{rT} \cdot \frac{X_{BT}}{X_B}. \quad (7)$$

As the concentration approaches zero, the calculated reduced viscosity and the true (target) reduced viscosity approach the calculated  $[\eta]^*$  and true (target)  $[\eta]$  intrinsic viscosities, respectively. Equation (7) then becomes

$$[\eta]^* = [\eta]_T \cdot \frac{X_{BT}}{X_B}. \quad (8)$$

Using the Mark-Houwink relationship, intrinsic viscosity can be expressed as a function of molecular weight for both the true (target) and the calculated intrinsic viscosities:

$$[\eta]^* = K(M)^*_a \quad (9)$$

$$[\eta]_T = K(M)_T^a \quad (10)$$

where  $(M)^*$  and  $(M)_T$  are the calculated and true molecular weights, respectively. Substituting (9) and (10) into (7), it can be easily shown that

$$(M)^* = (M)_T \left[ \frac{X_{BT}}{X_B} \right]^{1/a} \quad (11)$$

The true bulk concentration can be expressed as a relative function of the target concentration by eq. (12):

$$\phi = \frac{X_B}{X_{BT}}. \quad (12)$$

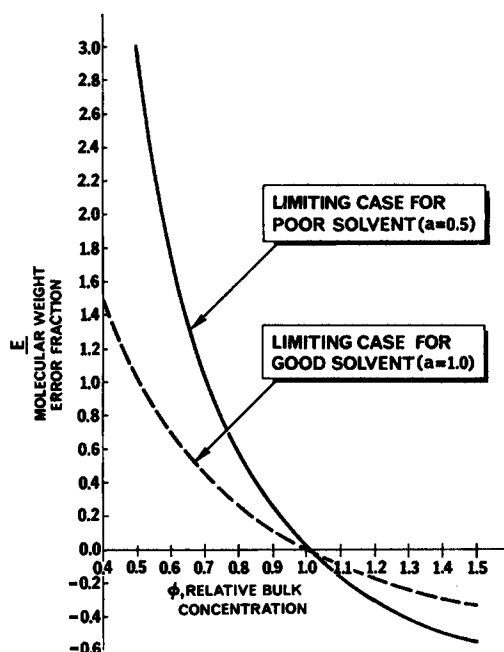


Fig. 1. Variation of the error in calculated molecular weight as a function of the true/target bulk solution concentrations.

Substituting (12) into (11) and rearranging, we obtain

$$\frac{(M)_*}{(M)_T} = \phi^{-1/a}. \quad (13)$$

The error fraction  $E$  is defined by eq. (14) in terms of the calculated molecular weight and the true (target) molecular weight:

$$E = \frac{(M)_* - (M)_T}{(M)_T}. \quad (14)$$

Substituting (13) into (14), the desired expression is obtained:

$$E = \phi^{-1/a} - 1. \quad (15)$$

Equation (15) shows that the error fraction for molecular weight is a function of the power-law exponent of the Mark-Houwink relation and, therefore, will vary with the nature of the polymer-solvent interaction. For linear macromolecules in good solvents, the value of  $a$  approaches unity. In a poor solvent where the polymer is only sparingly soluble, the value<sup>2</sup> of  $a$  approaches 0.5. For these limiting cases, eq. (15) reduces to (16) and (17), which are also shown in Figure 1:

Good solvent: 
$$E = \frac{1 - \phi}{\phi} \quad (16)$$

Poor solvent: 
$$E = \frac{1 - \phi^2}{\phi^2} \quad (17)$$

### CONCLUSIONS

Molecular weight values determined from intrinsic viscosity measurements are very sensitive to errors in concentration. An equation was derived which expresses the error in calculated molecular weight as a function of the relative deviation of concentration from a target value. The relation shows that the error is smaller if the true concentration is higher than the target value and if the polymer is in a good solvent rather than a poor one.

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### References

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