

# NOTE

## Degradation Index Calculation from Viscometry Data

### INTRODUCTION

To determine quantitatively the degradation extent of a polymer, it is necessary to measure the changes of its molecular weight. Among the methods available for measuring the molecular weight, the most simple and accessible one that is available to every laboratory is the dilute solution viscometry (DSV) technique. The DSV yields the intrinsic viscosity  $[\eta]$ , from which the value of viscosity-average molecular weight,  $M_v$ , may be calculated using the Mark-Houwink-Sakurada (MHS) equation:

$$[\eta] = K \cdot M_v^a,$$

The exponent  $a$  depends on the extent of interaction between the polymer and the solvent used in DSV.

When the polymer studied has the most probable distribution (MPD), then the following relation is true:

$$M_{no}/M_n = M_{vo}/M_v \quad (1)$$

Hence, the degradation index (DI) may be calculated from intrinsic viscosity changes:

$$DI = (M_{no}/M_n) - 1 = ([\eta]_o/[\eta])^{1/a} - 1 \quad (2)$$

If the initial molecular weight distribution (MWD) is different from MPD, then Eq. (1) is incorrect, since the ratio  $M_v/M_n$  (viscosity-polydispersity) is variable. In such a case, the correlation between  $[\eta]$  and DI is complex and an accurate picture is unknown at the present. In ref. 1 it was proposed to describe the viscosity changes by means of an approximate equation:

$$[\eta]/[\eta]_o = A \cdot (DI + 1)^{n-a} \quad (3)$$

where  $A$  and  $n$  are constants dependent on the MHS exponent  $a$  and molecular weight distribution shape. Equation (3) is valid only in a limited range of DI values.<sup>1</sup> In this article the approach of Chee<sup>1</sup> has been extended. The coefficients  $A$  and  $n$  proposed here enable an increase in the range of DI values, where Eq. (3) may be applicable. In addition, the selected coefficients are linearly dependent

on the MHS exponent  $a$  and the weight-polydispersity  $P_{wo} = M_{wo}/M_{no}$  of the initial molecular weight distribution. Consequently, the obtained parameter values may be expressed by two simple equations.

### EXPERIMENTAL PROCEDURE

In ref. 1 the validity of Eq. (3) was assessed on the basis of  $[\eta]$  predictions' uncertainty. Apparently, it is more reasonable to estimate the inaccuracy of the DI calculation, since Eq. (3) is used in practice to determine DI from viscometry experimental data. A precise correlation between degradation index and intrinsic viscosity changes had been obtained by Monte Carlo computer simulation.<sup>2</sup> The simulations quoted have an inaccuracy maximum of less than 0.5%. Then values of DI calculated from Eq. (3) at specific ratios of  $[\eta]/[\eta]_o$  were compared with the computer experimental data of DI at the same values of  $[\eta]/[\eta]_o$ . The deviations obtained in this way characterize the accuracy of predictions of DI by Eq. (3) and the accuracy of parameters  $A$  and  $n$ . Typical curves of approximation uncertainty for the Schulz distribution with  $P_{wo} = 4$  are demonstrated in Figure 1. For broad MWDs they are convex upward and for narrow MWDs they are concave downward. Figure 1 and Table I show that the parameters  $A$  and  $n$  have strong influences on these curves. If the maximum inaccuracy of the DI calculation is given (e.g., 10%), then the best values of the foregoing parameters may be selected for it.

### RESULTS

In this work several Schulz distributions with weight-polydispersity from 1 to 7 were investigated. For them, the data of uncertainty of approximation by Eq. (3) for many different pairs of values of  $A$  and  $n$  were obtained. As mentioned earlier, the screening of suitable parameters  $A$  and  $n$  had two purposes: (1) the inaccuracy of the DI determination must be less than 10%; and (2) the aforementioned parameters must be linearly dependent on the MHS exponent  $a$  and on the polydispersity  $P_{wo}$ . It was found that these two terms are inapplicable at narrow and broad distributions simultaneously. Therefore, more attention was concentrated on broad molecular weight distributions since they are frequently observed. The screening resulted in the following expressions:

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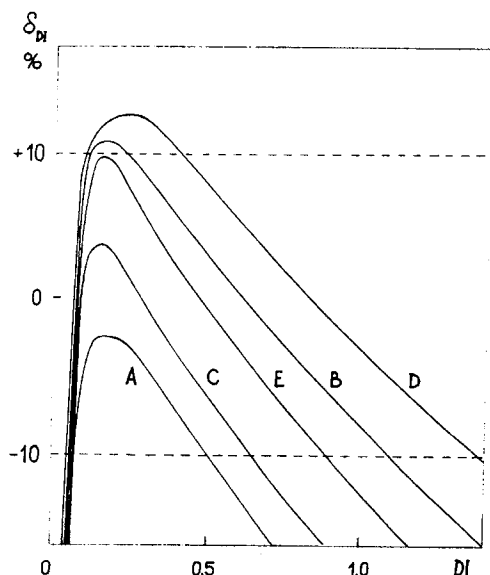
$$A = 1.01 - 0.005 \cdot P_{wo} \quad (4)$$

$$n = (0.5 \cdot a - 0.1) \cdot (2 - P_{wo})$$

At these values of  $A$  and  $n$ , Eq. (3) has the limits of applicability which are shown in Figure 2. On the left, the area of validity of Eq. (3) is limited by the value of  $P_{wo} = 1.5$ . The narrower molecular weight distributions are rare. For broad MWDs, two areas of invalidity exist. The first one is at low DI's: from zero to about 0.05. The upper limit of success of Eq. (3) is dependent on the exponent  $a$  (see Fig. 2). The area of validity may be extended if the maximum permissible uncertainty is established on a higher level. For comparison, in Figure 2 the validity limit of Eq. (3) with parameters  $A$  and  $n$  from ref. 1 has been shown by a broken line.

## CONCLUSION

The dependence of intrinsic viscosity on DI has been proposed as



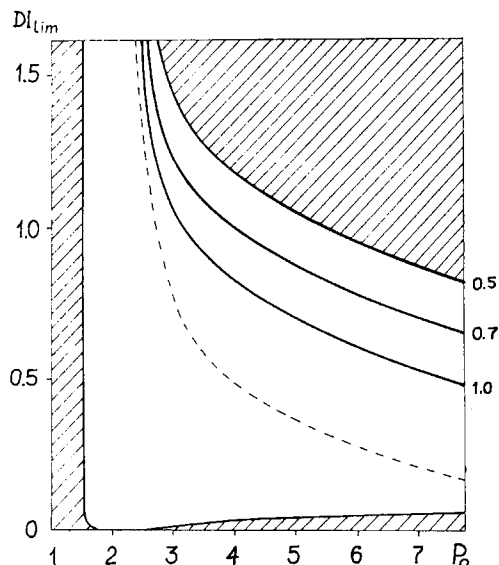
**Figure 1** The typical plots of uncertainty of DI calculation for initial Schulz distribution with  $P_{wo} = 4$  at diverse values of parameters  $A$  and  $n$  which have been listed in Table I;  $a = 0.7$ .

**Table I** Values of Parameters  $A$  and  $n$  for the Plots from Figure 1

| Line Code | $A$   | $n$     |
|-----------|-------|---------|
| A         | 0.991 | -0.294* |
| B         | 0.986 | -0.45   |
| C         | 0.991 | -0.56   |
| D         | 0.981 | -0.40   |
| E         | 0.990 | -0.50** |

\* Values from ref. 1.

\*\* Values according Eq. (4).



**Figure 2** The area of validity of Eq. (3) at values of parameters  $A$  and  $n$  according to Eq. (4). The figures near the curves mark the values of the MHS exponent.

$$[\eta]/[\eta]_0 = (1.01 - 0.005 \cdot P_{wo}) \times (DI + 1)^{0.1 \cdot P_{wo} - 0.5 \cdot a \cdot P_{wo} - 0.2}$$

Hence the degradation index may be calculated from changes of intrinsic viscosity by means of the following expression:

$$DI = \left\{ \frac{([\eta]/[\eta]_0)}{(1.01 - 0.005 \cdot P_{wo})} \right\}^{1/(0.1 \cdot P_{wo} - 0.5 \cdot a \cdot P_{wo} - 0.2)} - 1 \quad (5)$$

At  $P_{wo} = 2$  (the case of MPD), Eq. (5) becomes Eq. (2). On the basis of Figure 2 data for broad initial MWDs, this equation is suitable for use in a range of DI values from 0.1 to 0.5.

## REFERENCES

1. K. K. Chee, *J. Appl. Polym. Sci.*, **41**, 985 (1990).
2. A. V. Shyichuk and V. S. Lutsjak, *Ukr. Khim. Zhurn.*, **59**, 219.

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