How to Measure the Degradation Index by Viscometry

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SYNOPSIS

To calculate the degradation index (DI) from the intrinsic viscosity changes, a simple and accurate enough equation has been proposed: $DI = \{([\eta]_0/[\eta])^{1/a} - 1\}/(0.57 \times P_{w0} - 0.14)$, with P_{w0} being the initial polydispersity index: $P_{w0} = M_{w0}/M_{n0}$. The inaccuracy of the DI determination caused by the experimental inaccuracy of intrinsic viscosity measurements was evaluated to be larger at low values of the Mark–Houwink exponent. The determination is more accurate when the initial MWD is broad. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

To study the process of polymer degradation, it is necessary to know the number of main-chain scissions. It may be easily calculated from the changes of the number-average molecular weight:

$$N_s = 1/M_n - 1/M_{n0} \qquad (1)$$

Here, N_s is the scissions concentration (mol/kg) and M_{n0} and M_n are, respectively, the initial and final values of the number-average molar mass (kg/mol). The dimensionless relative parameter degradation index (DI) is also used to characterize quantitatively the polymer degradation process. DI is equal to the average number of scissions per initial number-average macromolecule:

$$DI = N_s/N_0 = N_s \times M_{n0} = M_{n0}/M_n - 1 \qquad (2)$$

where N_0 is the initial concentration of macromolecules (mol/kg). At the same time, the viscosity-average molecular weight, M_v, is of interest in determining the degradation extent because the dilute solution viscometry (DSV) technique is reliable and has low expense. The calculation of the DI from viscometry data is simple in the case of the Flory initial distribution. In that case, the ratio M_v/M_n is constant and, consequently,

$$DI = M_{v0}/M_v - 1 \qquad (3)$$

Combining eq. (3) with the Mark–Houwink (MH) equation

$$[\eta] = K \times M_v^a$$

leads to

$$DI = ([\eta_0]/[\eta])^{1/a} - 1 \qquad (4)$$

Here, $[\eta]$ is the intrinsic viscosity and K and a are constants. The MH exponent a has a value in the range of 0.5–1.0. If the initial MWD differs from the Flory distribution, eqs. (3) and (4) are incorrect because the distribution shape and ratio M_v/M_n are variable under polymer degradation. Despite this, many experimental works on polymer degradation are carried out using viscometry measurements and eqs. (3) and (4), by assuming that the initial MWD is the Flory distribution. That way, undoubtedly, has an inaccuracy which increases with increasing the difference between the initial and the Flory distributions.

Different theoretical approaches to the relationship between the DI and the intrinsic viscosity considering the MWD breadth are known.[1–6] In ref. 1, a broad initial MWD was introduced as a superposition of two Flory distributions, and, further, the calculations were performed for both distributions separately. By using the theory described in ref. 2, an approximate equation was derived in ref. 3. The equation was improved[4] to extend the area of its

validity. In refs. 5 and 6, the relationship in question was precisely determined using the Monte Carlo simulation. Accurate equations were obtained[5,6] which describe the intrinsic viscosity dependence on the degradation degree (DD):

$$DD = \ln(M_{n0}/M_n)$$

These equations have the relative inaccuracy of the DD predictions, which is less than 1.5% for narrow MWDs[5] and 2% for the broad ones.[6] Unfortunately, the equations are transcendental and one cannot calculate the DD from the intrinsic viscosity changes by algebraic methods. Those computations may be performed only by numerical methods with a computer.

Thus, accurate correlation between the intrinsic viscosity and DD is now known. On the other hand, in a real measuring experiment, the intrinsic viscosity data have a certain experimental inaccuracy. The measurements' inaccuracy affects the resulting value of the DD. For that reason, the objects of this work are (1) to estimate the inaccuracy value of the predictions of the degradation extent caused by the primary inaccuracy of the intrinsic viscosity measurements and (2) to estimate the inaccuracy of the simple eq. (3) caused by the MWD shape and to compare it with the aforementioned experimental inaccuracy.

EXPERIMENTAL

For the convenience of comparison, the following discussion uses the DI parameter. It was simply correlated with both the scission number and the DD (see above).

First, to evaluate the DI inaccuracy, it is necessary to know the inaccuracy of the primary experimental parameter, i.e., the intrinsic viscosity. The relative inaccuracy of the intrinsic viscosity measurements is equal to ca. 1–3%.[7] The value of 2% was accepted in the present study. Second, the derivative of the DI dependence on the intrinsic viscosity is necessary for the evaluation.[8] The derivative was obtained numerically from the data of the Monte Carlo simulations described in refs. 5 and 6. Next, the absolute inaccuracy of the DI determination (Δ_{DI}) was calculated:

$$\Delta_{DI} = (d\mathrm{DI}/d\mathrm{IV}) \times \Delta_{IV}$$

with ($d\mathrm{DI}/d\mathrm{IV}$) being the derivative, and Δ_{IV}, the absolute inaccuracy of the intrinsic viscosity. Fur-

ther, the relative inaccuracy, δ_{DI}, was obtained: $\delta_{DI} = \Delta_{DI}/\mathrm{DI}$.

The inaccuracy of eq. (3) was evaluated by comparing the equation predictions directly with the computer simulation data. The treatment was performed with the software package QUATTRO PRO 4.0.

RESULTS

The results concern the case of random chain scission. All the obtained data were investigated depending on the MH exponent value, on the DI value, and on the breadth of the initial MWD:

1. *The inaccuracy of the DI determination caused by the experimental inaccuracy of the intrinsic viscosity measurements* is displayed in Figure 1. It is apparent that the inaccuracy has a large value in the initial stage and decreases greatly at a larger DI. That is clear as at small DIs even a minor absolute DI deviation leads to a large value of the DI relative inaccuracy. Figure 1 also shows a great effect of the breadth of the initial MWD. In the case of a broad initial MWD, the viscosity-average molecular weight decreases with a larger rate than in the case of a narrow MWD. Consequently, when the initial MWD is broad, then the derivative $d\mathrm{DI}/d\mathrm{IV}$ has a lesser value and the relative inaccuracy is also less. Figure 2 demonstrates the effect of the MH exponent a. It can be seen that the less the MH ex-
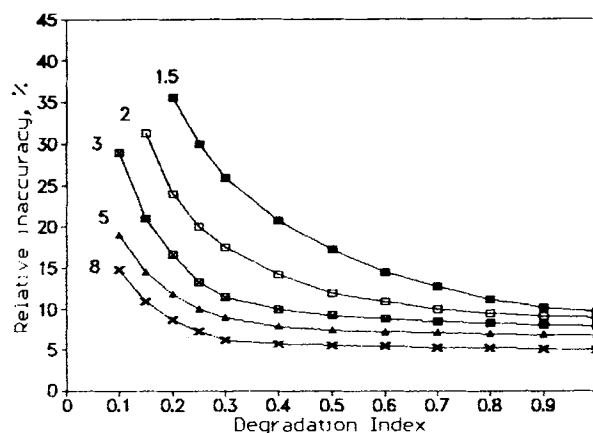

Figure 1 Relative inaccuracy of the DI determination caused by the intrinsic viscosity measurements' inaccuracy, which is equal to 2%. The MH exponent is equal to unity. The numbers near the curves mark the initial polydispersity index.
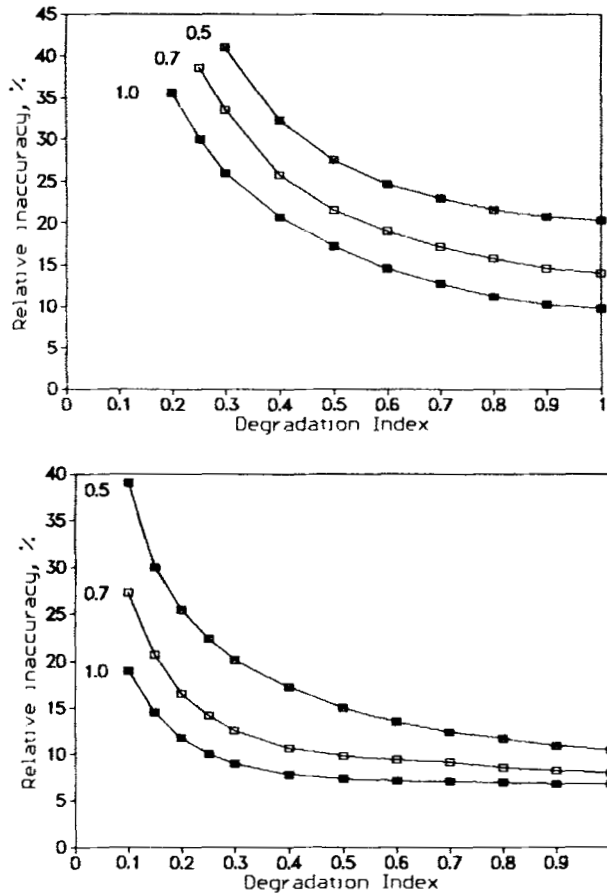
Figure 2 Relative inaccuracy of the DI determination caused by the intrinsic viscosity measurements' inaccuracy at $P_{w0} = 1.5$ (a) and $P_{w0} = 5$. The numbers near the curves mark the MH exponent value.

Figure 3 Relative inaccuracy of eq. (3) predictions at the following parameters: (■) $P_{w0} = 5$, $a = 1.0$; (□) $P_{w0} = 5$, $a = 0.5$; (⊠) $P_{w0} = 4$, $a = 1.0$; (×) $P_{w0} = 4$, $a = 0.5$; (▲) $P_{w0} = 1.5$, $a = 1.0$; (+) $P_{w0} = 1.5$, $a = 0.5$.

ponent the larger is the DI inaccuracy. In addition, at low MH exponent values, the effect of the initial MWD breadth remains the same as in the case $a = 1$ [compare Fig. 2(a) and 2(b)].

Thus, determinations of the DI by viscometry will be more accurate when the initial MWD is broad and $a = 1$. The displayed data may be directly used to evaluate the DI determinations' inaccuracy when real experiments are performed. If the real inaccuracy of the intrinsic viscosity measurements differs from the value 2%, then the proportional correction must be introduced into the scale of the inaccuracy axis.

2. *The inaccuracy of eq. (3)* is shown in Figure 3. It can be seen that for different initial MWDs the inaccuracy has diverse values. For initial broad MWDs, the inaccuracy is a pos-
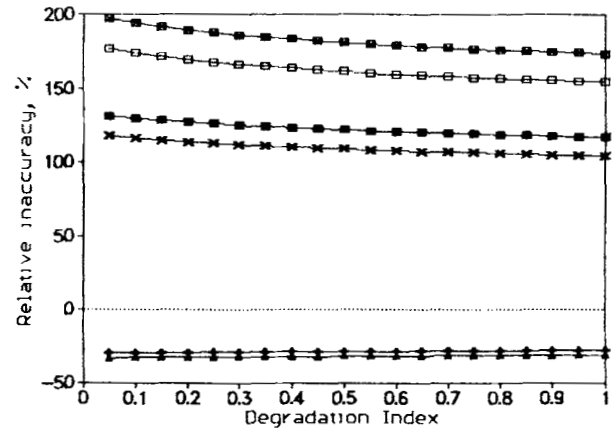
itive quantity, and for the narrow ones, it is negative. For the Flory initial distribution, the inaccuracy is equal to zero. Comparison of Figure 3 with Figure 1 shows that the inaccuracy of eq. (3) may be much larger than that caused by the experimental measurements' inaccuracy. It is clear that eq. (3) cannot be applied to MWDs with the polydispersity index beyond the range 1.5–2.5.

At the same time, the inaccuracy in question remains almost unchanged with an increasing DI (see Fig. 3). That feature makes it possible to correct the eq. (3) predictions by an adjustable parameter:
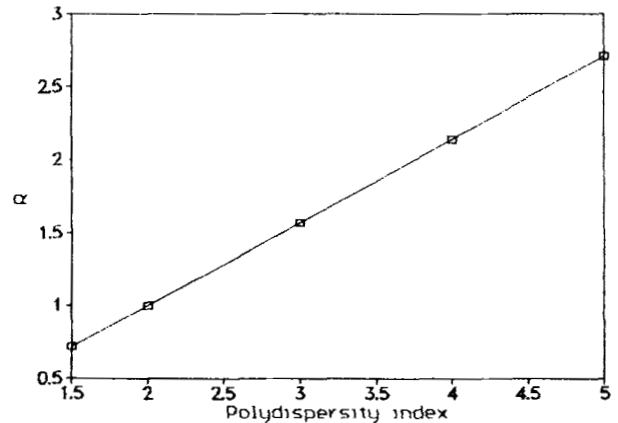
$$DI = (M_{v0}/M_v - 1)/R$$

Figure 4 Parameter R vs. the polydispersity index.

The performed screening shows that the most suitable values of parameter R are linearly correlated with the initial MWD polydispersity (see Fig. 4). The correlation was found as

$$R = 0.57 \times P_0 - 0.14$$

with P_{w0} being the initial polydispersity index: $P_{w0} = M_{w0}/M_{n0}$. At $P_{w0} = 2$, the R value is equal to unity. Hence, the corrected equation was obtained:

$$DI = (M_{v0}/M_v - 1)/(0.57 \times P_{w0} - 0.14) \quad (5)$$

That equation is already accurate enough (see Fig. 5). The relative inaccuracy of eq. (5) is less than the one caused by the inaccuracy of the intrinsic viscosity measurements (compare with Fig. 2). Considering the MH equation, one can write
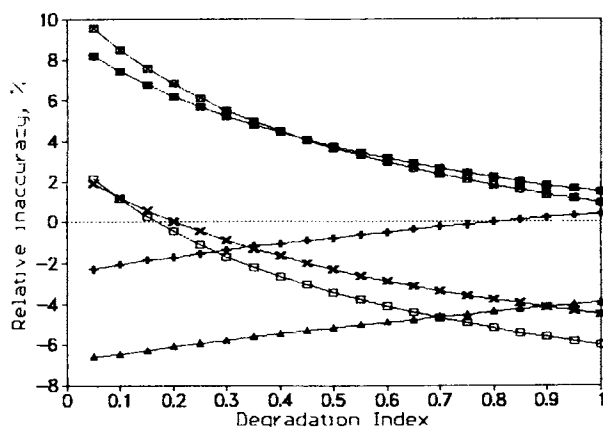

Figure 5   Relative inaccuracy of eq. (5) predictions. The signs are the same as in Figure 3.

$$DI = \{ ([\eta]_0/[\eta])^{1/a} - 1 \}/(0.57 \times P_{w0} - 0.14)$$

CONCLUSION

The simple eqs. (3) and (4) cannot be used for the determination of the degradation extent because of a very large inaccuracy: about 100–200%. To determine the DI from the intrinsic viscosity measurements, it is recommended to use the refined eq. (5). It is also recommended to take the solvent with a large value of the MH exponent and the polymer with a broad MWD. The data of Figures 1 and 2 may be directly used to assess the DI determination inaccuracy in real experiments.

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