Accurate Description of Intrinsic Viscosity Changes Under Polymer Degradation: Narrow Schulz Distributions

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SYNOPSIS

For the Shulz distributions with weight-polydispersity from 1.4 to 2.0, the following equation is correct: $\ln[\eta] = \ln[\eta]_0 - a\{\ln P_0 + DD - \ln[P_F - (P_F - P_0) \times \exp(-1.2 \times DD)]\}$. Here, P_0 and P_F are viscosity-polydispersities of the initial molecular weight distribution (MWD) and the Flory distribution, respectively; a is the Mark–Houwink exponent; and $DD = \ln(M_{n0}/M_n)$. For more narrow MWDs, the complicated equation is required: $\ln[\eta] = \ln[\eta]_0 - a\{\ln P_0 + DD - \ln[P_F - (P_F - P_0) \times \exp(-0.9 \times DD - 0.28 \times DD^2)]\}$. The inaccuracy of these equations is less than 1.5%. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It is of great practical interest to know the correlation between intrinsic viscosity and the degradation extent of a polymer sample in order to be able to measure the degradation degree of the polymer using an easy viscometry technique. This correlation is simple in the particular case of the Flory distribution (most probable distribution, MPD):

$$[\eta]/[\eta]_0 = (M_v/M_{v0})^a = (M_n/M_{n0})^a \qquad (1)$$

At the same time, the above-mentioned correlation is fairly complex if the initial molecular weight distribution (MWD) differs from the MPD. An analytical approach to the problem solution encounters difficulties and yields approximate results.[1,2] In this conjunction, it is reasonable to take advantage of computer simulation. So, the method applied in Ref. 3 makes it possible to compute the intrinsic viscosity changes in the case of broad MWD, and the algorithm described in Ref. 4 is workable for both broad and narrow MWDs. The computer program yields intrinsic viscosity, weight-average and z-average molecular weights, and the full picture of the MWD changes under polymer degradation.[4] It is known that many real polymers have MWDs of the Schulz–Zimm type.[5] Therefore, it is of interest to find regularities of the intrinsic viscosity degradative changes for the initial Schulz–Zimm distributions. It is also desirable to present the generalized results in the compact form of an equation. Reference 6 proposed the approximate equation describing intrinsic viscosity changes:

$$[\eta]/[\eta]_0 = (1.01 - 0.005 \times P_{w0}) \times (DI + 1)^{0.1\times P_{w0} - 0.5\times a\times P_{w0} - 0.2}$$

where P_{w0} is the initial value of the weight-polydispersity, a is the Mark–Houwink exponent, and the degradation index (DI) $= M_{n0}/M_n - 1$. This equation is the refined form of the one given in Ref. 2. They both have restricted validity ranges.[2,6] A most precise approximation has been reached in the present article. This is due to the use of the new parameter of degradation degree:

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

The parameter DD was proposed in Ref. 7 as the one having an additivity property unlike the DI. Two empirical equations were derived here, which precisely describe the correlation between intrinsic viscosity and DD. The equations concern the narrow Schulz distributions which have a weight-polydispersity, M_w/M_n, of less than 2.

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EXPERIMENTAL

The correlation equations were derived on the basis of Monte Carlo computer experiments. An algorithm and details of the computations were described in Refs. 4 and 6. The Schulz MWD is expressed by the formula

$$q_n(u) = z^{b+1} \times u^b \times \exp(-z \times u)/\Gamma(b+1)$$

where $q_n(u)$ is the numerical fraction of molecules with the polymerization degree u; b and z, the parameters determining polydispersity and M_n; and $\Gamma(x)$, the gamma function of x. In the present work, six distributions with diverse coefficients b were investigated (Table I). Also, respectively, they have diverse polydispersities:

$$M_w/M_n = (b+2)/(b+1) \qquad (2)$$

Table I shows good agreement between the polydispersities calculated from the MWD under the computer experiments and those predicted by eq. (2).

The changes of MWD were simulated by the Monte Carlo model.[6] The initial distribution is presented in the computer memory as an array of the numbers which are weight fractions of molecules with specific molecular weights. The elementary act of scission is performed in the following way: The program takes a random macromolecule and cuts it up. The scission location is performed at random as well. Further, the program executes a corresponding alteration of the MWD. The scission probability is the same for every monomer unit. Simulations were executed at six values of the Mark–Houwink (MH) exponent a (0.5, 0.6, 0.7, 0.8, 0.9, and 1.0), i.e., 36 computer experiments have been carried out. The validity of the simulation results was certified by means of the formula which yields the weight-average polymerization degree changes under random degradation[8]:

$$u_2'' = u_2 - 3^{-1} y u_3 u_2 + 12^{-1} y^2 u_4 u_3 u_2 - \cdots$$
$$+ 2(-1)^i (i+2)!^{-1} y^i u_{i+2} u_{i+1} \cdots u_2 + \cdots \qquad (3)$$

Here, y is the scission density; u_2 and u_2'', the initial and final values of the weight-average polymerization degree; and u_3 is the initial value of the z-average polymerization degree, etc. Deviations of the simulated values from the eq. (3) predictions are very slight (see Fig. 1). There is no doubt that viscosity-average molecular weight data also have such high precision.

Table 1 Parameters of Initial MWDs

MWD Code	b	Weight-polydispersity Experimental	Weight-polydispersity Theoretical
A	4.9	1.169	1.169
B	2.0	1.333	1.333
C	1.4	1.416	1.416
D	0.7	1.588	1.588
E	0.4	1.713	1.714
G[a]	0.2	1.830	1.833

[a] The letter F has been reserved for the Flory distribution.

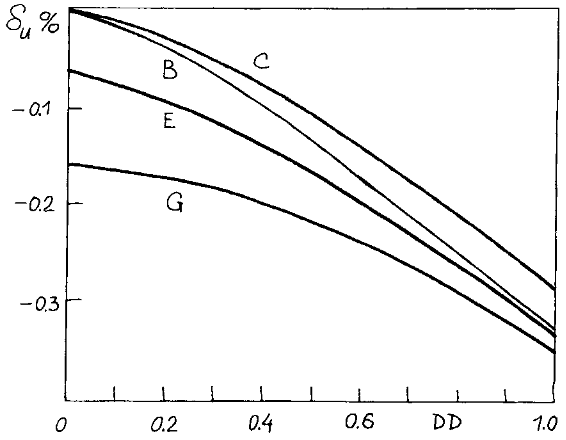

Figure 1 The inaccuracy of Monte Carlo computations of the weight-average molecular weight changes under polymer degradation.

RESULTS

First Approximation

The computer experiments yielded the precise dependencies of the viscosity–polydispersity $P = M_v/M_n$ upon DD. Some of them are shown in Figure 2. One can see that in all the cases the P value gradually approaches a certain limit which is the polydispersity of the Flory distribution and depends upon the MH exponent value:

$$P_F = (\Gamma(a+2))^{1/a} \qquad (4)$$

So, it is reasonable to transform the primary results to the form $(P_F - P)$ vs. DD. The plots obtained in this way are well rectiable in logarithmic scale (see Fig. 3). Here, only the plots of the very narrow distributions are slightly convex upward. In the first

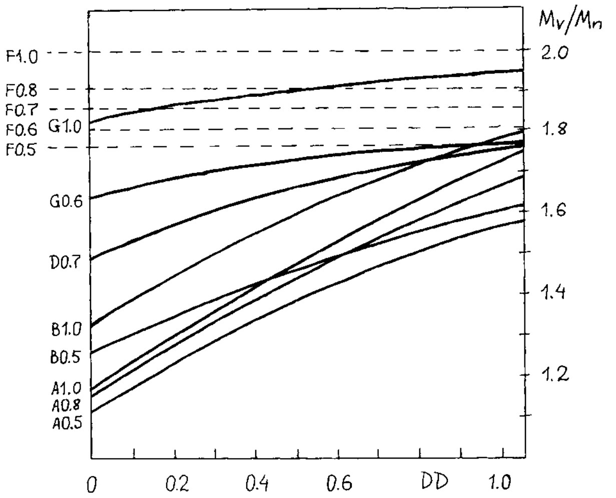

Figure 2 Dependence of viscosity–polydispersity upon *DD* for some the distributions. The letter notation coincides with that in Table I. The numerical code designates the Mark–Houwink (MH) exponent value.

approximation, one can allow that all the plots in Figure 3 are straight lines:

$$\ln(P_F - P) = \ln(P_F - P_0) - S \times DD$$

with the same slope $S = 1.2$. With this allowance, one can write

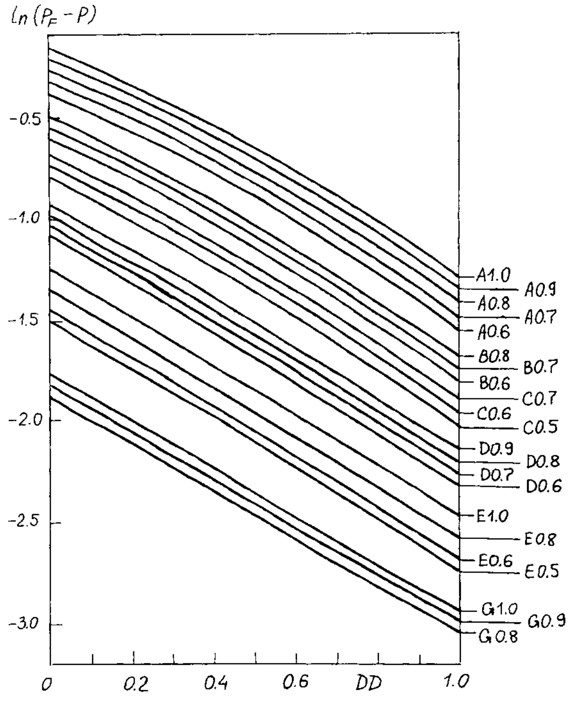

Figure 3 Transformed experimental data.

$$\ln M_v = \ln M_{n0} - DD$$
$$+ \ln[P_F - (P_F - P_0) \times \exp(-1.2 \times DD)].$$

Combination of this expression with the MH equation

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

yields

$$\ln[\eta] = \ln[\eta]_0 - a(\ln P_0 + DD - \ln[P_F - (P_F - P_0) \times \exp(-1.2 \times DD)] \quad (5)$$

If the initial MWD is an MPD (i.e., $P_0 = P_F$), then eq. (5) turns into

$$\ln[\eta] = \ln[\eta]_0 - a \times DD$$

which is equal to (1). To estimate the inaccuracy of eq. (5) predictions, the values of the intrinsic viscosity according to (5) were calculated and compared with the computer-simulated ones at the corresponding *DD* values. Figure 4 demonstrates the comparison results. It can be seen that eq. (5) is accurate enough, and only for the very narrow distributions does the inaccuracy value become approximately equal to the average experimental inaccuracy of dilute solution visometry technique (about 3%). On the other hand, the practical significance of eq. (5) consists of the possibility of the *DD* value determination from the intrinsic viscosity measurement data. Therefore, it is also reasonable to assess the *DD* estimation inaccuracy. From eq. (5), one can compute the *DD* value by the Newton iterative method if the $[\eta]$ and $[\eta]_0$ values are known.

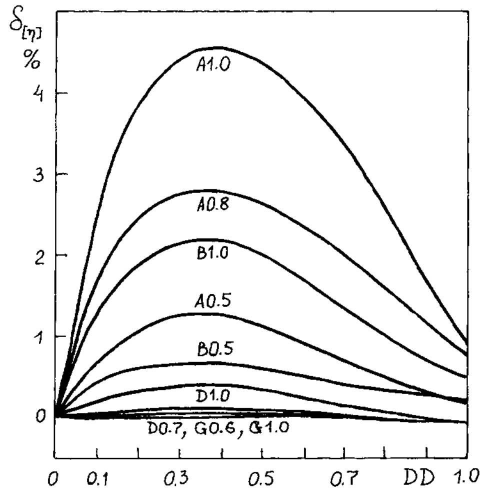

Figure 4 The inaccuracy of intrinsic viscosity calculation by eq. (5).

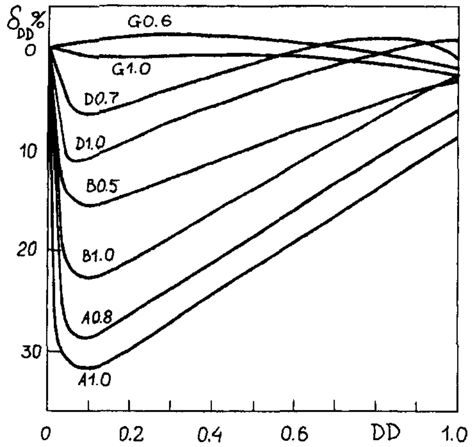

Figure 5 The inaccuracy of DD computation by eq. (5).

These computations were performed for all MWDs studied at various conversion degrees and the obtained DD values were compared with the DD values from computer simulation. Relative differences between them are displayed in Figure 5. It is seen that the DD prediction inaccuracy decreases at low values of the MH exponent a (as well as the intrinsic viscosity predictions accuracy—Fig. 4). Comparison of Figures 4 and 5 also shows that the DD prediction inaccuracy is more than the one of the intrinsic viscosity. This difference is particularly pronounced at small degrees of degradation because of the relative character of the parameter DD: At a low conversion degree, even a minor deviation of the estimated DD value is comparable with the low real DD value. Considering the Figure 5 data, for distributions D, E, and G, one can assume eq. (5) to be fairly accurate. Also, for very narrow MWDs, it is necessary to search for a more accurate expression.

Refined Approximation for the Very Narrow Distributions

Plots A, B, and C in Figure 3 are markedly convoluted. To describe such a curve line by a precise function, it is necessary to know its slope at every point in the investigated DD range (from 0 to 1.0). Slopes of the above-mentioned plots were calculated. It was found that the dependencies of the slope S upon DD for the considered MWDs are almost straight (see Fig. 6). Thus,

$$S = S_0 + SS \times DD \tag{6}$$

where S_0 is the initial slope value and SS is the proportionality coefficient. The numerical values of S_0 and SS are listed in Table II. As a matter of fact, slope S is a derivate of the function $\ln(P_F - P)$:

$$S = -d[\ln(P_F - P)]/dDD$$

Hence, one can write

$$d[\ln(P_F - P)]/dDD = -S_0 - SS \times DD \tag{7}$$

Integration of (7) yields

$$\ln(P_F + P) = C_0 - S_0 \times DD - 0.5 \times SS \times DD^2$$

where C_0 is the integration constant. In the present case, C_0 is equal to $\ln(P_F - P_0)$. As the values of coefficients S_0 and SS remain almost unchanged (Table II), they can be accepted as the constants with averages:

$$S_0 = 0.9$$

$$SS = 0.56.$$

With this assumption, the final expression is

$$\begin{aligned}\ln[\eta] = \ln[\eta]_0 - a\{&\ln P_0 + DD \\ &- \ln[P_F - (P_F - P_0) \\ &\times \exp(-0.9 \times DD - 0.28 \times DD^2)]\}\end{aligned} \tag{8}$$

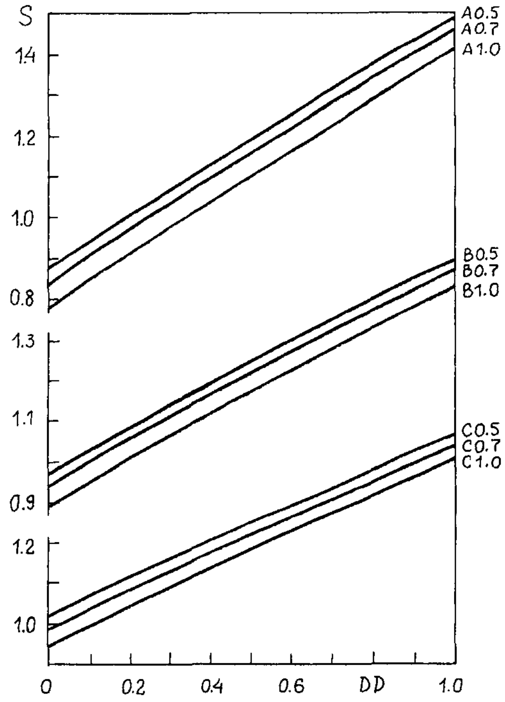

Figure 6 The dependence of the slope S upon DD.

The inaccuracy of the *DD* predictions by eq. (8) was determined by the above-described procedure and it is demonstrated in Figure 7(a). A more refined approximation may be obtained if the exact values of S_0 and *SS* are used individually for the every pair of MWD and the MH exponent, but this is not necessary. The inaccuracy of the intrinsic viscosity predictions by eq. (8) [see Fig. 7(b)] is less than the average experimental inaccuracy of the DSV technique (~ 3%) and, therefore, the deviations of the *DD* predictions by eq. (8) are less than the *DD* determination inaccuracy which results from the experimental inaccuracy. Thus, eq. (8) is recommended to be used for the Schulz distributions with initial weight–polydispersity from 1 to 1.4.

CONCLUDING REMARKS

Equations (5) and (8) include the parameters P_F and P_0 which are viscosity–polydispersities. The P_F value may be calculated at the specific value of the MH exponent by formula (4) with the gamma function[9]; however, another way exists. It has been remarked[10] that the *P* value is a linear function of the MH exponent. For the Flory distribution, the following equation is correct:

$$P_F = 1.5334 + 0.4666 \times a \qquad (9)$$

In the case that the P_0 value is unknown but the initial value of weight–polydispersity P_{w0} is known, then the former may be calculated by

$$P_0 = P_{w0} + 0.4666 \times (P_{w0} - 1) \times (a - 1) \qquad (10)$$

Finally, for the narrow Schulz distributions, eqs. (5) and (8) in conjunction with eqs. (9) and (10) make it possible to calculate the intrinsic viscosity degradative changes and, vice versa, to determine the *DD* from the data of the intrinsic viscosity measurement.

Table II Values of Eq. (6) Parameters

Experiment Code	S_0	*SS*
A1.0	0.785	0.633
A0.9	0.803	0.637
A0.8	0.821	0.636
A0.7	0.839	0.638
A0.6	0.826	0.635
A0.5	0.883	0.631
B1.0	0.895	0.554
B0.7	0.945	0.544
B0.5	0.979	0.543
C1.0	0.948	0.484
C0.7	0.993	0.472
C0.5	1.025	0.457

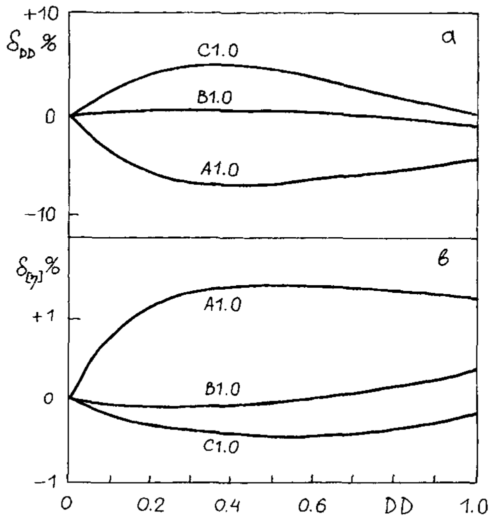

Figure 7 The inaccuracy of (a) the *DD* computation and (b) the [η] calculation by eq. (8).

REFERENCES

1. A. M. Kotliar, *J. Polym. Sci.*, **51,** S63 (1961).
2. K. K. Chee, *J. Appl. Polym. Sci.*, **41,** 985 (1990).
3. M. A. Zhuravlev and N. G. Taganov, *Vysokomol. Soedin.*, **B32,** 142 (1990).
4. A. V. Shyichuk and V. S. Lutsjak, *Ukr. Khim. Zhurn.*, **59,** 216 (1993).
5. G. V. Schulz, *Z. Phys. Chem.*, **B43,** 25 (1939).
6. A. V. Shyichuk, *J. Appl. Polym. Sci.*, to appear.
7. A. V. Shyichuk, *Ukr. Khim. Zhurn.*, **57,** 1229 (1991).
8. A. Charlesby, *Atomic Radiation and Polymers,* Part 9, Pergamon press, Oxford, 1960.
9. *Table of the Gamma Function for Complex Arguments,* U.S. Government Printing Office, Washington, DC, 1954.
10. K. K. Chee, *J. Appl. Polym. Sci.*, **30,** 1359 (1985).

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