

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

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SYNOPSIS

For the Schulz broad distributions with initial weight-polydispersity from 2 to 10, the correlation between the intrinsic viscosity and the degradation degree, $DD = \ln(M_{n_0}/M_n)$, has been found as the following equation system: $\ln[\eta] = \ln[\eta]_0 - \alpha(\ln P_0 - \ln P + DD)$; $P = P_F + (P_0 - P_F) \times \exp((S_0 - 1.43)(\exp(-S \times DD) - 1)/SS - 1.43 \times DD)$; $S_0 = 0.33 + 0.557 \times P_{w_0}$; $SS = 1.962 + 0.9428 \times \ln(P_{w_0} - 1)$. Here P_0 , P , and P_F are viscosity-polydispersities: initial, current, and that of the Flory distribution, respectively. This correlation inaccuracy has been assessed to be about 2%. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Research on the polymer degradation and stabilization requires many measurements of the polymer degradation degree. In order to cut down the expenses it is reasonable to use the simple and reliable dilute-solution viscometry technique. The parameters degradation index (DI) and degradation degree (DD) may be calculated easily from the intrinsic viscosity changes in the case of the initial Flory distribution:

$$DI = M_{n_0}/M_n - 1 = ([\eta]_0/[\eta])^{1/\alpha} - 1$$

$$DD = \ln(M_{n_0}/M_n) = \alpha^{-1} \times \ln([\eta]_0/[\eta])$$

The empirical equations correlating intrinsic viscosity changes with DD have been obtained on the basis of computer simulation data for narrow molecular weight distributions (MWDs) of the Schulz-Zimm type.¹ On the other hand broad MWDs are more frequently observed in research practice. In the present paper the cited approach has been applied successfully to Schulz broad MWDs which have initial weight-polydispersity 2 to 10.

EXPERIMENTAL

The Schulz molecular weight distributions were calculated with the formula

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

Here $q_n(u)$ is numerical fraction of molecules with the polymerization degree u ; b and z are the parameters determining polydispersity and number-average molecular weight value. $\Gamma(x)$ is the gamma function of x . Polydispersities of simulated MWDs agree very well with the theoretical predictions (see Table I). The simulation of broad MWDs requires to define a very large array of numbers. Because of the limited volume of the computer memory, the high-molecular wing of MWD was cut off and therefore some polydispersities from the computer experiments are less than the theoretical ones. The algorithm of the simulation of random chain scission has been described in detail in ref. 2 and tested in ref. 1.

RESULTS

At first we shall consider the weight-average molecular weight data treatment. During the simulation of polymer chain scission the values of polydispersity of the studied MWDs decrease steeply and approach a specific limit, which is the polydispersity of the Flory distribution and equal to 2 (Fig. 1). This result is in complete agreement with the general theory of polymer degradation.³ Considering the above fact, it is reasonable to transform the primary experimental data to the form $\ln(P_w - 2)$ versus DD . That transformation has been made in previous work¹ and it has displayed itself as relevant. In the present

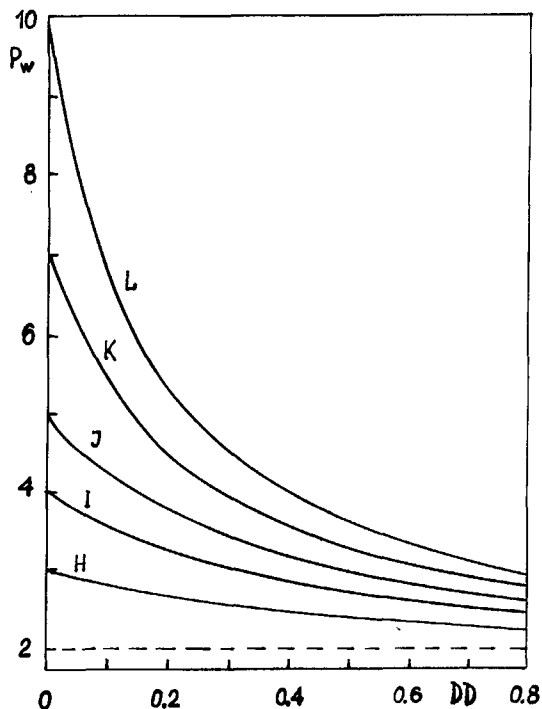
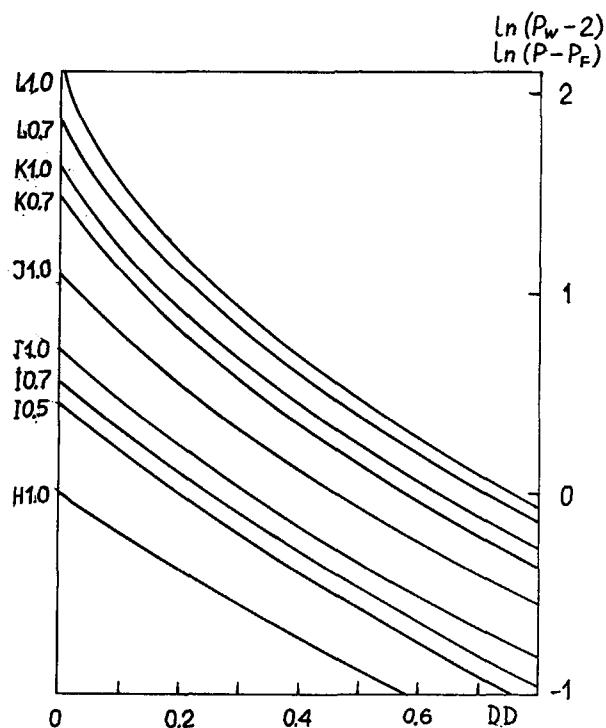
Table I Parameters of Initial MWDs

MWD Code	b	Weight-Polydispersity	
		Theoretical	Experimental
H	-0.5	3.000	2.989
I	-0.6666	3.999	3.990
J	-0.75	5.000	4.990
K	-0.8333	6.999	6.976
L	-0.8888	9.999	9.936

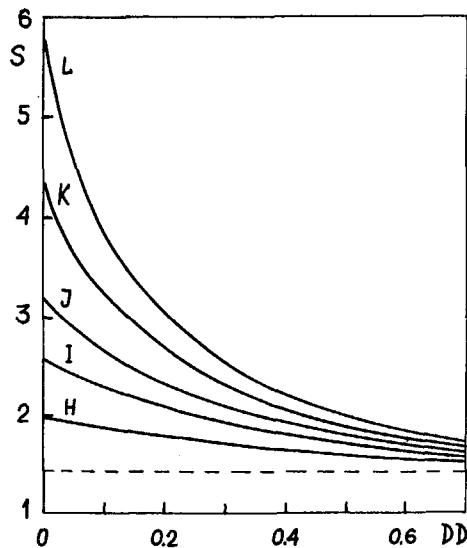
case the plots obtained in the above way are markedly convoluted (see Fig. 2). For that reason the linear approximation, unlike that in ref. 1, leads to a large inaccuracy, up to 25%, of the weight-average molecular weight predictions. In order to describe precisely the above plots, it is necessary to know their slopes in the studied range of the DD values. Slopes S have been calculated and displayed in Figure 3. The obtained graphs again are curvilinear. Further, these curves look like exponential ones, displaced along the axis of S :

$$S - C_d = (S_0 - C_d) \times \exp(-SS \times DD), \quad (1)$$

where C_d is the displacement constant, S_0 is the initial slope value, and SS is a certain proportionality

**Figure 1** Weight-polydispersity vs. degradation degree. Here and below the letter codes mark initial MWDs.**Figure 2** Transformation of primary data of computer experiments. The numbers near letterical codes indicate the Mark-Houwink exponent value.

coefficient. It has been found by screening that Figure 3 data satisfies eq. (1) at $C_d = 1.43$ quite well. This value has been displayed in Figure 3 by the broken line. The almost rectilinear plots of $\ln(S - 1.43)$ versus Degradation Degree (Fig. 4) validate eq. (1) and the adjustable parameter value. The computed values of S_0 and SS are listed in Table II.

**Figure 3** Slopes S vs. degradation degree.

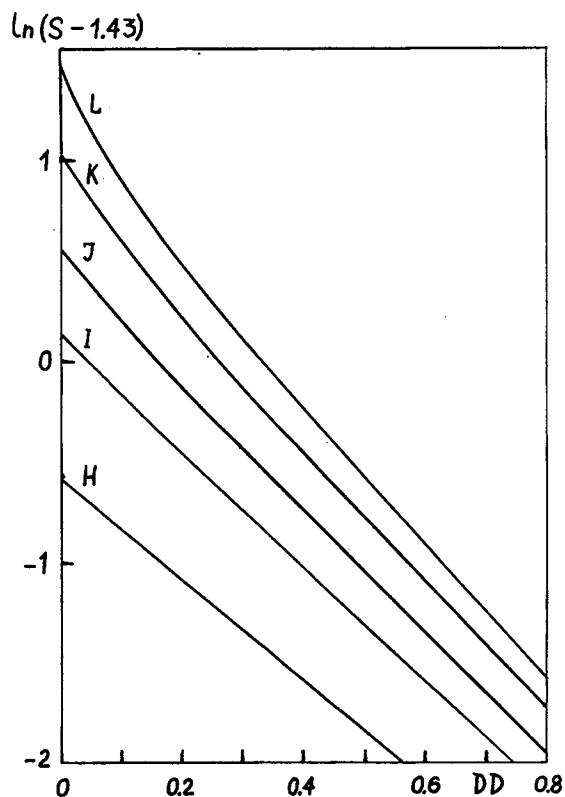


Figure 4 Treatment of experimental data according eq. (1).

As a matter of fact, parameter S is the derivative of the dependence studied:

$$S = -d \ln(P_w - 2) / dDD \quad (2)$$

Combining eqs. (1) and (2) yields

$$\begin{aligned} d \ln(P_w - 2) \\ = -(1.43 + (S_0 - 1.43) \times \exp(-SS \times DD)) \times dDD \end{aligned}$$

Integration of this expression results in

$$\begin{aligned} \ln(P_w - 2) &= -\int 1.43 dDD - (S_0 - 1.43) \\ &\quad \times \int \exp(-SS \times DD) dDD \\ &= -1.43DD - (S_0 - 1.43)(-1/SS) \\ &\quad \times \exp(-SS \times DD) + C_0 \end{aligned}$$

The integration constant C_0 depends on the initial conditions. At $DD = 0$ one can write

$$\ln(P_{w_0} - 2) = (S_0 - 1.43)/SS + C_0$$

from which follows

$$C_0 = \ln(P_{w_0} - 2) - (S_0 - 1.43)/SS$$

On balance, the following equation has been obtained:

$$\begin{aligned} \ln(P_w - 2) &= \ln(P_{w_0} - 2) - (S_0 - 1.43)/SS \\ &\quad + (S_0 - 1.43) \times \exp(-SS \times DD) / SS - 1.43DD \end{aligned}$$

and respectively

$$\begin{aligned} P_w &= 2 + \exp(\ln(P_{w_0} - 2) \\ &\quad + (S_0 - 1.43)(\exp(-SS \times DD) - 1) / \\ &\quad SS - 1.43DD) \quad (3) \end{aligned}$$

Verification of eq. (3) has displayed that the equation describes fairly accurately the M_w changes under degradation: deviations from the computer experiments data do not exceed 1%. Together with P_{w_0} , which is weight-polydispersity of initial MWD, eq. (3) includes parameters S_0 and SS , whose values depend on P_{w_0} (see Table II). To handy calculating it is desirable to represent S_0 and SS as functions of P_{w_0} . It has been proven that the parameter S_0 has the linear dependence on P_{w_0} [Fig. 5(a)], which may be expressed by the following formula:

$$S_0 = 0.33 + 0.557P_{w_0} \quad (4)$$

As to parameter SS , the dependence on P_{w_0} becomes rectilinear only in the specially selected coordinates [Fig. 6(b)]:

$$SS = 1.962 + 0.9428 \ln(P_{w_0} - 1) \quad (5)$$

Thus, eqs. (3), (4), and (5) taken together make it possible to predict the M_w changes under degradation of a polymer with Schulz initial MWD which is broader than the Flory distribution. For calculation it is necessary to know the initial value of weight-polydispersity of the polymer, P_{w_0} .

Viscosity-average molecular weight changes are expected to be similar to weight-average molecular weight ones because M_w is the particular case of M_v .

Table II Values of Eq. (6) Parameters

MWD Code	S_0	SS
H	1.977	2.511
I	2.576	2.916
J	3.164	3.193
K	4.263	3.651
L	5.784	4.132

Vis-polydispersity of a degrading polymer also tends to the constant value, which is vis-polydispersity of the Flory distribution, P_F . The P_F value depends on the MH-exponent a :¹

$$P_F = 1.5334 + 0.4666 \times a \quad (6)$$

The transformation of the M_v experimental data to the form $\ln(P - P_F)$ vs. DD has displayed that the modified data are highly similar to those of M_w (Fig. 2), and only coefficients S_0 and SS differ slightly. For that reason the following equation has been proposed for the description of vis-polydispersity changes under degradation:

$$P = P_F + \exp(\ln(P_0 - P_F) + (S_0 - 1.43) \times (\exp(-SS \times DD) - 1) / (SS - 1.43 \times DD)) \quad (7)$$

with S_0 , SS , and P_F according to eqs. (4)–(6). Value of $P_0 = M_{v0}/M_{n0}$ may be measured experimentally or calculated¹:

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

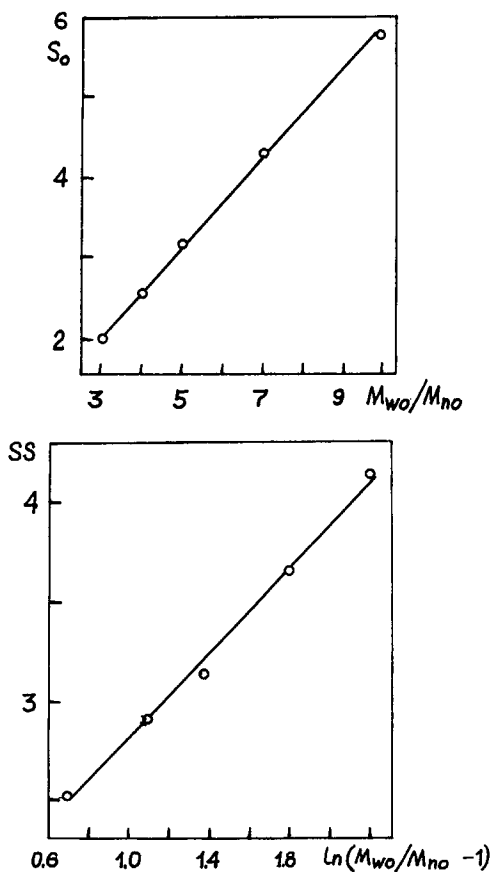


Figure 5 Correlation of S_0 (a) and SS (b) with initial weight-polydispersity.

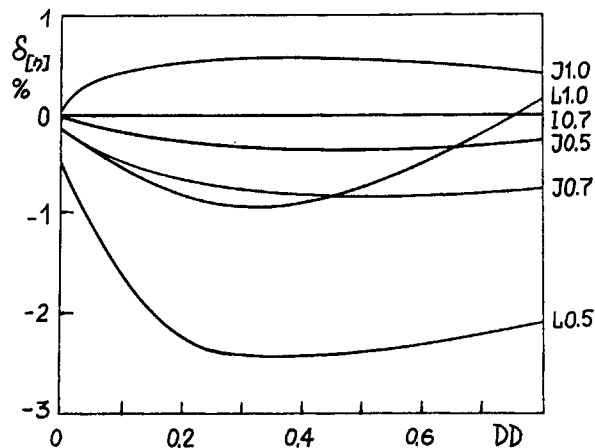


Figure 6 Relative inaccuracy of intrinsic viscosity predictions according to eqs. (7) and (8).

Since the current value of vis-polydispersity, P , is now known, then the intrinsic-viscosity changes may be calculated:

$$\frac{[\eta]}{[\eta]_0} = \left(\frac{M_v}{M_{v0}}\right)^{1/a} = \left(\frac{P}{M_n} \times \frac{M_{n0}}{P_0}\right)^{1/a} \quad (8)$$

The results of intrinsic viscosity computations from eqs. (7) and (8) correspond quite well to the primary data of the computer experiments (see Fig. 6). A substantial inaccuracy has been found only for very broad distributions but suchlike ones are rarely observed.

CONCLUSION

In the case of Schulz broad distribution the intrinsic viscosity changes under degradation may be calculated by means of eqs. (4)–(8). For the computation it is necessary to know only the initial polydispersity and the MH-exponent value. The inaccuracy of the computation is less than the experimental error of intrinsic viscosity measurements (average 3%). The obtained dependences may be applied to the DD determination from viscometry data.

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