

# Relation Between Intrinsic Viscosity and Molecular Weight

H. M. QUACKENBOS, *R&D Laboratories, Union Carbide Corporation, Bound Brook, New Jersey 08805*

## Synopsis

The connection between intrinsic viscosity and number-average and weight-average molecular weight has been revealed by calculations from distribution curves. Log-normal distributions, and moderate variations thereon, were chosen as typical for polystyrene and other thermoplastics. Intrinsic viscosity and number-average molecular weight are unlikely to be related because of the highly disturbing effect of small variations in molecular weight distribution. Conversely, intrinsic viscosity is a good practical measure of weight-average molecular weight up to a ratio of 10 for weight-to-number average.

## INTRODUCTION

The relation between intrinsic viscosity  $[\eta]$  and molecular weight  $M$  was first expressed by Staudinger as

$$[\eta] = KM \quad (1)$$

where  $K$  is a constant. Later, the equation was modified to the form

$$[\eta] = KM^a \quad (2)$$

where  $a$  is a constant with a value that is often about 0.7 in a good solvent. This is usually called the Mark-Houwink equation and sometimes the Mark-Houwink-Sakurada equation.

When this equation is applied, a strong distinction is usually made between fractions and whole resins. For narrow fractions the ratio of weight-average to number-average molecular weight,  $M_w/M_n$ , approaches the monodisperse ideal of 1.0. A plot of molecular weight, determined by light scattering etc., versus intrinsic viscosity is linear on logarithmic coordinates. From the plot,  $K$  and  $a$  can be readily determined. Conversely, for the whole resin  $M_w/M_n$  may be 2.0 or considerably higher. The values of  $K$  and  $a$  are usually considered to be no longer strictly valid, and intrinsic viscosity then expresses a vague "viscosity average" molecular weight, one that lies between  $M_w$  and  $M_n$ .

The second restriction on this equation is that it is valid only for linear polymers with short side chains. If long-chain branching (LCB) is present, as in some low-density polyethylenes, the relationship becomes invalid. For such a polyethylene fractionated in this laboratory, our log-log plot of molecular weight by light scattering versus intrinsic viscosity had a pronounced curvature. The points for the fractions at the low end were nearly linear; here LCB was minimal. For higher fractions, LCB was more prominent and molecular weight rose rapidly in comparison with intrinsic viscosity. At the highest intrinsic viscosity of 2.8, the linear extrapolation of the points at the low end suggested a molecular weight

of about 200,000. The actual value was over 3 million. The converse of this situation is incorporated in the well-known Billmeyer estimate for LCB—in terms of the ratio of the intrinsic viscosity expected for a similar linear polymer with no LCB to the actual intrinsic viscosity. Because of these complications, polymers with LCB are excluded from the following treatment.

The vague domain of the polydisperse resin is the subject of this article. Looking for useful approximations we examine polydisperse resins ranging widely in width of molecular weight distribution,  $M_w/M_n$  being varied from 2 to 15. In this range can intrinsic viscosity be an approximate measure of either  $M_n$  or  $M_w$ ?

### EXPERIMENTAL

The method proceeds by calculation. A reasonable distribution of molecular weight (and intrinsic viscosity) is assumed. From the distribution we calculate  $M_w$ ,  $M_n$ , and  $[\eta]$ .

To illustrate, consider the distribution curve of Figure 1 for resin A. It is concave upward in logarithmic normal coordinates, with intrinsic viscosity varying from 2.6 at 99.5% cumulative wt % down to 0.052 at 0.5%. To determine the corresponding molecular weight we assume that the resin is polystyrene with a Mark-Houwink relation<sup>1</sup>:

$$[\eta] = 6.82 \times 10^{-3} M^{0.77} \quad (3)$$

determined for narrow fractions. Molecular weight  $M$  in eq. (3) was measured by light scattering and was actually  $M_w$ , though presumably it was within a few percent of  $M_n$ . Intrinsic viscosity was run in tetrahydrofuran at 23°C. For  $[\eta] = 0.052$  the molecular weight can be calculated as 5800.

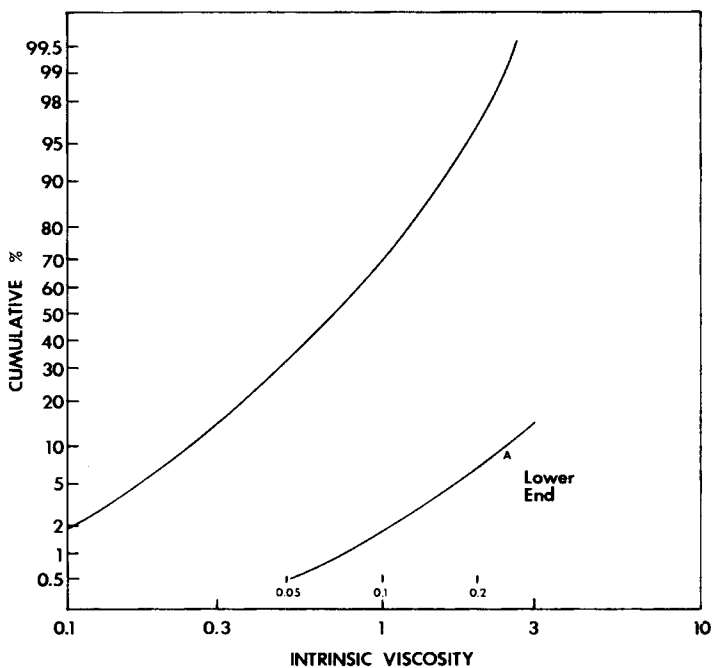


Fig. 1. Distribution curve for A.

The resin of Figure 1 was divided into 16 fractions with center points listed in Table I. For the whole resin intrinsic viscosity was calculated from the simple additive rule:

$$[\eta] = w_1[\eta]_1 + w_2[\eta]_2 + \dots$$

where  $[\eta]_1$  is the intrinsic viscosity of fraction 1 of weight fraction  $w_1$ , etc. The summation of Table I yields for the whole resin an intrinsic viscosity of 0.812.

Similarly, molecular weights were calculated from the classical relations

$$M_w = w_1M_1 + w_2M_2 + \dots$$

$$1/M_n = w_1/M_1 + w_2/M_2 + \dots$$

In summary (Table I), the resin in Figure 1 has the following calculated values:

$$[\eta] = 0.812$$

$$M_w = 210,500$$

$$M_n = 85,000$$

$$M_w/M_n = 2.48$$

These are typical for a commercial polystyrene or the matrix of an impact polystyrene.

In the first calculations, we divided the resin into 27 pieces but found that with 16 coarser cuts, as in Table I, the calculated results changed less than 1%. In the middle of the distribution, where intrinsic viscosity is changing slowly, fine cuts are not needed; a 10% cut is sufficient, for example, between 58 and 68%

TABLE I  
Calculation of Intrinsic Viscosity and Molecular Weights<sup>a</sup>

% Center point	$W_i$	$[\eta]_i$	$W_i [\eta]_i$	$M_i$	$W_i M_i$	$10^5 W_i / M_i$
0.5	0.01	0.052	—	5,800	~100	0.172
1.5	0.01	0.091	0.001	11,500	~100	0.087
3	0.02	0.132	0.003	19,000	400	0.105
6	0.04	0.19	0.008	30,000	1,200	0.133
13	0.10	0.28	0.028	50,000	5,000	0.200
23	0.10	0.40	0.040	79,000	7,900	0.127
33	0.10	0.50	0.050	106,000	10,600	0.094
43	0.10	0.62	0.062	140,000	14,000	0.071
53	0.10	0.74	0.074	175,000	17,500	0.057
63	0.10	0.88	0.088	219,000	21,900	0.045
73	0.10	1.06	0.106	278,000	27,800	0.036
83	0.10	1.30	0.130	360,000	36,000	0.028
90	0.04	1.56	0.062	455,000	18,200	0.009
94	0.04	1.75	0.071	530,000	21,200	0.007
97	0.02	2.04	0.041	640,000	12,800	0.003
99	0.02	2.40	0.048	790,000	15,800	0.003
			0.812		210,500	1.177

<sup>a</sup> For whole resin:  $[\eta] = 0.812$ ;  $M_w = 210,500$ ;  $1/M_n = 1.177/10^5$  and  $M_n = 85,000$ ;  $M_w/M_n = 2.48$ .

centered at 63%. Fine cuts are necessary only at the sensitive ends of the distribution. For the fraction centered at 1.5%, for example, the fineness of the cut may be judged from a calculation that  $M_w/M_n$  is 1.02, the fraction being further subdivided into 10 pieces to establish this ratio.

Similar calculations were made for two distributions resembling those of Figure 1 but having a parallel displacement. In one distribution the intrinsic viscosity at any cumulative percent was 1.5 times that of the original; in the other it was 0.5 times. For such parallel displacement a total recalculation is not necessary because it can be shown that for the "1.5 resin" the values for the original are multiplied as follows:

$$\begin{aligned} \text{intrinsic viscosity} &= 1.5 \\ M_n, M_w &= 1.5^{(1/a)} \text{ or } 1.693 \end{aligned}$$

where  $a$  is the exponent in eq. (2) and is 0.77 (eq. 3). The three results of Table II were obtained in this way.

## RESULTS

Four more distributions shown in Figure 2 were treated in the same way, with results summarized in Table III. Three types are covered in terms of the log normal distribution pattern—concave, linear, and convex. Note the spread of  $M_w/M_n$  from 2 to 15.

### Shape Variation

The intrinsic viscosities and the molecular weights from Table III are presented on a log-log plot in Figure 3 along with the Mark-Houwink line (M-H) as a reference.

The principal features of Figure 3 are the following:

(1) For a given family of constant shape and constant  $M_w/M_n$ , like A, for example, both molecular weights are linear in intrinsic viscosity and the line has the same slope as the M-H line for narrow fractions.

(2) The lines for  $M_w$  lie to the right of the reference line, meaning that the value for  $M_w$  is higher for a whole resin than expected from the M-H line. Yet the displacement is not excessive. At intrinsic viscosity = 1.0 the M-H equation gives a value of 260,000 for  $M_w$ , while the worst line passes through 330,000, a shift of about 30%. Thus for the whole resins not exceeding a moderate breadth of distribution, the reference M-H equation allows a good approximate prediction

TABLE II  
Concave Distributions of the Type of Figure 1

$[\eta]$ for whole resin	$M_n^a$	$M_w^a$	$(M_w/M_n)$
0.812	85.0	210.5	2.48
1.218	143.0	354.2	2.48
0.406	34.6	85.6	2.48

<sup>a</sup> In thousands.

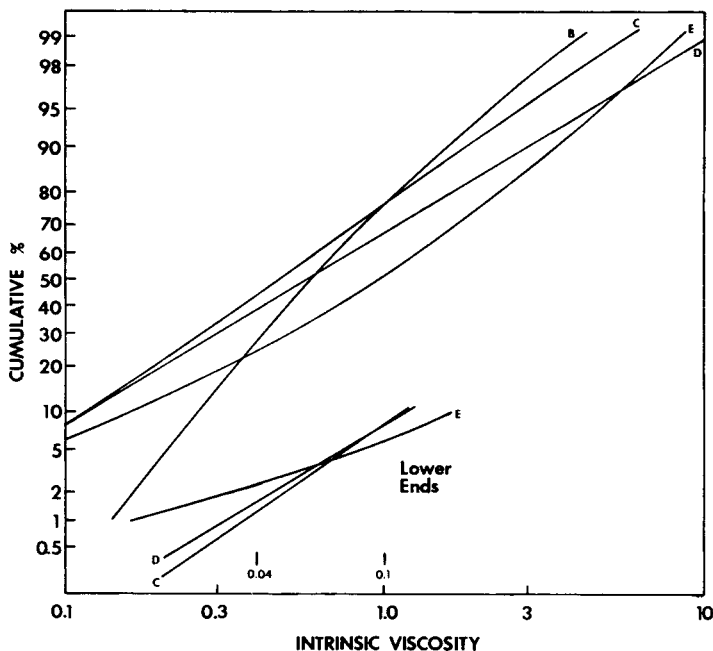


Fig. 2. Distribution curves for B, C, D, and E.

of  $M_w$  from intrinsic viscosity, the answer being low. The error tends to increase as  $M_w/M_n$  rises but depends also on the shape of the MWD curve.

(3) The lines for  $M_n$  lie to the left, yielding values at a given intrinsic viscosity lower than would be predicted from the reference equation. The degree of left displacement depends principally on  $M_w/M_n$  and may be almost independent of MWD contour. The shift in  $M_n$  can be exceptionally large. At intrinsic viscosity = 1.0 the  $M_n$  can be as low as 20,000, compared to 260,000 for the reference line.

TABLE III  
Summary of Calculated Results

Curve type <sup>a</sup>	$[\eta]$ for whole resin	$M_n^b$	$M_w^b$	$(M_w/M_n)$
B, Convex	0.797	106.0	214.1	2.02
	1.195	178.8	361.2	2.02
	0.398	43.1	87.0	2.02
C, Linear	0.812	37.8	235.8	6.24
	1.218	63.8	397.8	6.24
	0.406	15.4	95.9	6.24
D, Linear	1.154	38.8	394.8	10.2
	0.770	23.0	234.0	10.2
	0.385	9.3	95.1	10.2
E, Concave	1.49	33.0	511.0	15.5
	0.99	19.6	304.0	15.5
	0.50	8.0	124.0	15.5

<sup>a</sup> Shape of curve on a log-normal distribution plot.

<sup>b</sup> In thousands.

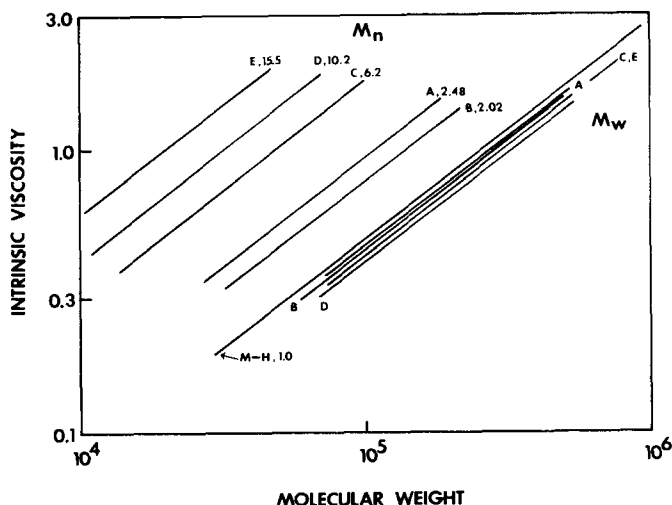


Fig. 3. Relationships between intrinsic viscosity and molecular weights. Number on line denotes  $M_w/M_n$ .

### Comparison with Kurata et al.

Of particular interest is an analysis by Kurata et al.<sup>2</sup> for "log normal distributions," those resembling our types C and D. By combining the previous equations for intrinsic viscosity and average molecular weights with an expression for a log-normal distribution, they solved the problem with mathematical rigor. Where there is an overlap in conclusions and implications, our findings and theirs agree that (1) if  $M_w/M_n$  remains constant, both  $\log M_w$  and  $\log M_n$  are linear in  $\log$  intrinsic viscosity with a slope equal to that of the M-H equation and (2) if  $M_w/M_n$  does not remain constant, the disturbance for  $M_w$  is much less than that for  $M_n$ .

They expressed their results as

$$[\eta] = K_n (M_n)^a \quad (4)$$

$$[\eta] = K_w (M_w)^a \quad (5)$$

where  $M_n$  for the whole resin is calculated using a different constant,  $K_n$ , from that ( $K$ ) in the M-H equation. A similar notation was used for  $M_w$ . Their neat treatment showed that

$$K_n/K = (M_w/M_n)^{0.5a(a+1)} \quad (6)$$

$$K_w/K = (M_w/M_n)^{0.5a(a-1)} \quad (7)$$

For  $a = 0.77$ , as here, we then have

$$K_n/K = (M_w/M_n)^{0.681}$$

$$K_w/K = (M_w/M_n)^{-0.088}$$

The variation of these two  $K$  ratios with  $M_w/M_n$  is given as two lines in Figure 4. The points represent results for our five families, A-E. Points and lines agree well for our two log-normal distributions C and D. The divergence for the other three points indicates some effect of MWD shape.

Actually, Kurata et al. applied their analysis in a limited way. They were

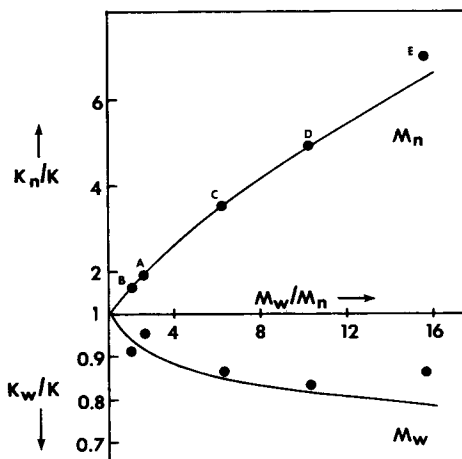


Fig. 4. Correction factors. Lines are for a log-normal distribution calculated from the equations of Kurata et al. Points are for resins A-E.

concerned only with the effect of overly broad functions on the purity of determination of  $K$  and  $a$  in the Mark-Houwink equation.

### Practical Applications to Thermoplastics

Figure 5 is a plot of intrinsic viscosity versus  $M_w$  for three of the distributions in Table III. The relationship is reasonably regular, with the points lying within  $\pm 10\%$  of the best line. Accordingly, intrinsic viscosity is a valid indicator of  $M_w$  for a fairly wide range of distributions.

The practical implications that follow are (1) for a new or experimental family of linear thermoplastics intrinsic viscosity can be taken as an index of  $M_w$ , even if individuals vary considerably in their width of molecular weight distribution; and (2) for a more established resin it seems unnecessary to go to the trouble of isolating fractions for determining the M-H relationship. A determination of  $M_n$  and  $M_w$  for, say, three individuals will give a "best line" from which intrinsic viscosity alone can be used to calculate  $M_w$  for other individuals.

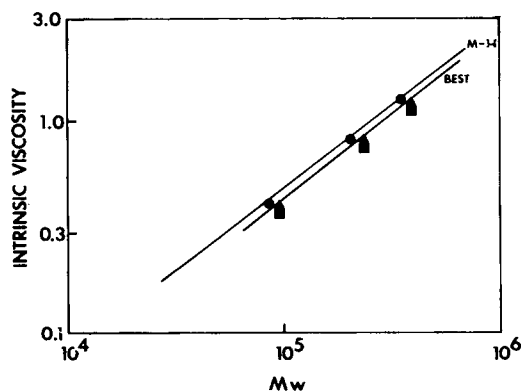


Fig. 5. Intrinsic viscosity vs.  $M_w$  for log-normal distributions: (●) A; (▲) C; (■) D.

While many thermoplastics fit in this framework, polymers with long-chain branching are excluded because of their complicating effect on intrinsic viscosity.

Although particular values of  $K$  and  $a$  have been used, the examples have general application. Variations of  $K$  have no effect, and only a minor influence is exerted as the value of  $a$  moves in the expected range from 0.7 to 0.8.

### References

1. K. A. Boni, F. A. Sliemers, and P. B. Stickney, *J. Polym. Sci. Part A-2*, **6**, 1579 (1968).
2. M. Kurata, Y. Tsunashima, M. Iwama, and K. Kamada, in *Polymer Handbook*, IV, 2nd ed., J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1975, pp. 1-4.

Received November 2, 1979

Revised December 19, 1979