

# A new representation of viscosity data as a function of molecular weight

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It is proposed to represent viscosity data by plotting  $1/[\eta]$  versus  $1/M^{1/2}$ . This gives a straight line even when the exponent  $a$  in the Mark–Houwink–Sakurada plot is not constant. The inverse of the slope of the straight line is approximately equal to  $K_\theta$ . The intercept determined by extrapolating the straight line plot to infinite  $M$  increases with the quality of the solvent.

Intrinsic viscosity index  $[\eta]$  is one of the most widely used parameters for the characterization of polymers. The relation between  $[\eta]$  and the molecular weight  $M$  of the polymer has been the object of many publications from both the theoretical and the experimental points of view. At the  $\theta$ -point the situation is clear because then the Mark–Houwink–Sakurada relation:

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

is obeyed with  $a = 0.5$ .

Relation (1) has been verified for a large range of molecular weights. For instance, Berry and Fox<sup>1</sup> and Altares *et al.*<sup>2</sup> have demonstrated the validity of this relation for polystyrene in cyclohexane at 35°C for molecular weights in the range from 500 up to a few millions.

When excluded volume effects are present the situation is much more difficult. The newer excluded volume theories<sup>3,4</sup> predict a relation between the radius of gyration  $R$  and  $M$  of the form,  $R^2 = K_1 M^\nu$  with  $\nu = 1.2$ . This implies a value of  $a = 0.8$  for an impermeable coil which, for instance, has not been observed in the case polystyrene–benzene. Moreover, in general, the exponent  $a$  can be considered as constant only for a narrow range of molecular weights.

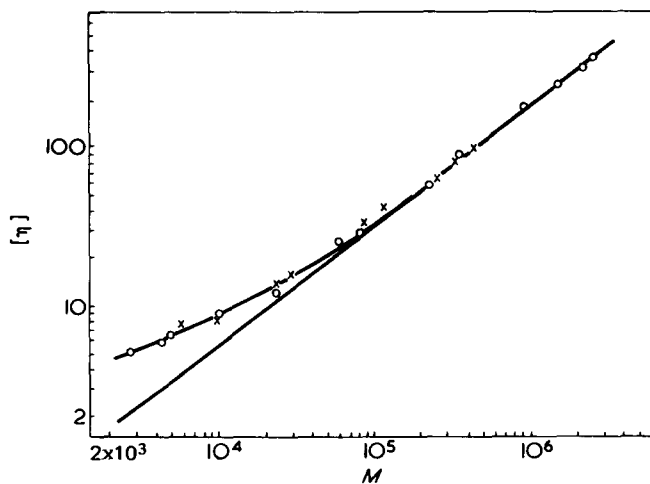


Figure 1 The Mark–Houwink–Sakurada relation for poly(methyl methacrylate) in benzene at 30°C: O, ref 9; X, present results

We have introduced<sup>5</sup> a new method of presenting viscosity data using the idea of segment concentration. This method seems to be generally applicable and particularly useful in the low and medium molecular weight range. A modification leading to a simpler presentation of the data is proposed.

Among methods to linearize the viscosity molecular weight relation, the best known is the Stockmayer–Fixman–Burchard plot<sup>6,7</sup>:

$$[\eta]/M^{1/2} = K_\theta + 0.51\phi_0 BM^{1/2} \quad (2)$$

where  $[\eta]/M^{1/2}$  is plotted as a function of  $M^{1/2}$ . It has been shown by Cowie<sup>8</sup> and others that this plot yields a linear relation only for molecular weights above about 40 000 and up to about 1 000 000.

The discussion presented in reference 5 suggests a plot of  $[\eta]^{-1}$  versus  $M^{-1/2}$ . Replacing  $[\eta]_\theta$  in the proposed relation<sup>5</sup>:

$$\frac{1}{[\eta]} - \frac{1}{[\eta]_\theta} = \Delta\rho = \Delta\rho_\infty - \frac{A'}{M^{1/2}} = -A_2 - \frac{A'}{M^{1/2}} \quad (3)$$

by  $K_\theta M^{1/2}$  we obtain

$$\frac{1}{[\eta]} = -A_2 + \frac{1}{K_\theta M^{1/2}} - \frac{A'}{M^{1/2}} = -A_2 + \frac{A_1}{M^{1/2}} \quad (4)$$

where  $A_1$  and  $A_2$  are constants. Equation (4) yields a straight line over a large domain of molecular weights as shown by a few examples.

The classical plot of  $\log [\eta]$  versus  $\log M$  for poly(methyl methacrylate) in benzene at 30°C is shown in Figure 1. The slope  $a$  varies from 0.5 to 0.76. The new plot gives the straight line shown in Figure 2. The experimental scatter is not larger than in the log–log plot and linearity is observed even for molecular weights down to 5000.

It is evident that this plot is only useful for the low and medium molecular weight range since at high molecular weights the points are crowded near the origin. Moreover, for an infinite molecular weight,  $[\eta]$  also has to be infinite. This is not borne out by equation (4). It is surprising to see that this linear relation is valid for a rather wide domain of molecular weights.

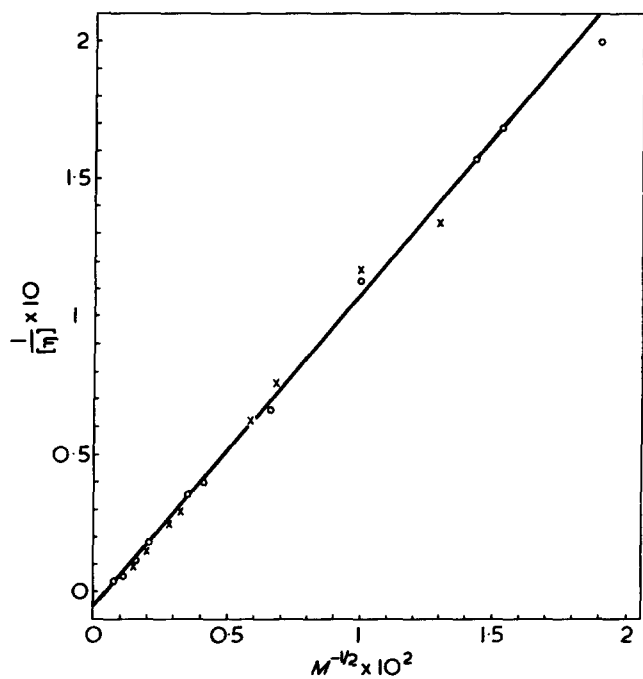


Figure 2 Plot of  $1/[\eta]$  versus  $1/M^{1/2}$  for poly(methyl methacrylate) in benzene at 30°C (Points as in Figure 1)

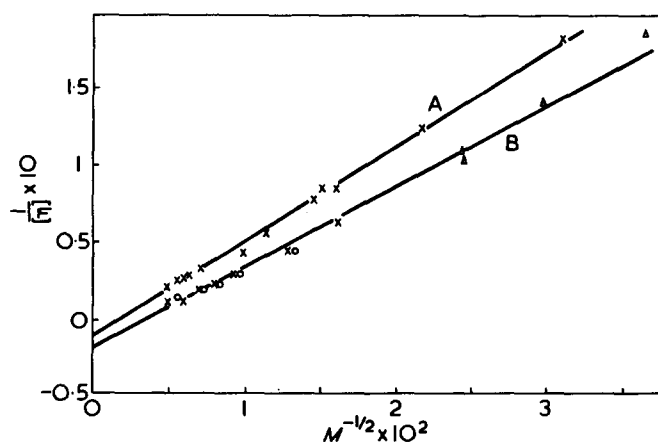


Figure 4 Plot of  $1/[\eta]$  versus  $1/M^{1/2}$  for poly(oxyethylene glycol) in dimethylformamide (A, ref 10) and chloroform (B: X, ref 11; O, ref 12; Δ, ref 13)

value appears to increase with the quality of the solvent. In all the experimental cases we have examined the parameter  $A_2$  is much smaller than  $A_1/M^{1/2}$  when  $M < 200\,000$ . This implies:

$$A_2 M^{1/2} \ll A_1 \quad (5)$$

With this approximation equation (4) can be rewritten as:

$$\frac{[\eta]}{M^{1/2}} = \frac{1}{A_1} + \frac{A_2}{A_1^2} M^{1/2} + \frac{A_2^2}{A_1^3} M + \dots \quad (6)$$

Thus, when the inequality (5) is obeyed, our equation (4) approaches the Stockmayer-Fixman-Burchard equation (equation 2) with  $A_1^{-1} = K_\theta$  and  $A_2/A_1^2 = 0.51\phi_0 B$ . Returning to equations (3) and (4) shows, however, that:

$$\frac{1}{A_1} = \frac{K_\theta}{1 - K_\theta A'} \quad (7)$$

It thus becomes understandable that in good solvents one often finds unperturbed dimensions which are larger than those observed at the  $\theta$ -point<sup>14</sup>.

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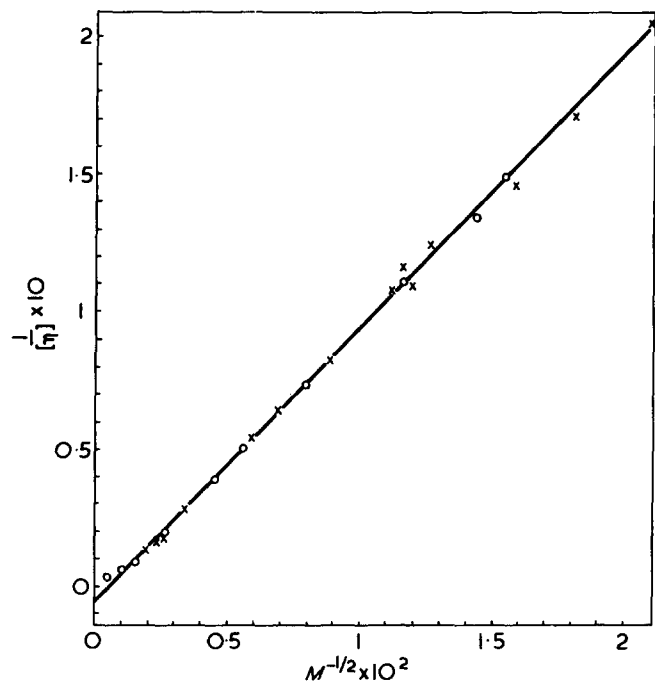


Figure 3 Plot of  $1/[\eta]$  versus  $1/M^{1/2}$  for polystyrene in benzene (x) and carbon tetrachloride (O) ( $T = 25^\circ\text{C}$ )

Figures 3 and 4 contain additional examples. Figure 3 represents data on polystyrene in benzene and carbon tetrachloride at 25°C obtained in our laboratory. Figure 4 shows data on poly(oxyethylene glycol) in dimethylformamide and chloroform<sup>10-13</sup> at 25°C. All these results lead to the same conclusion, viz. that equation (4) can be used over a broad range of molecular weights.

The parameter  $A_2$  is a measure of the goodness of the solvent and is evidently zero at the  $\theta$ -point. Its numerical