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Linear representation of viscosity data as a function of molecular weight: 2. Extension into the domain of high expansion coefficients

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In previous papers two new relations were proposed for a linear representation of the intrinsic viscosity of a polymer as a function of its molecular weight[1,2]. These relations were obtained by taking into account the difference in the segment density of the macromolecular coil at the Θ conditions and in the good solvent considered[3].

In this report we will try to extend the linear relation between the intrinsic viscosity and the molecular weight of a polymer in the domain of high molecular weights and high expansion coefficients. This is achieved by a modified Stockmayer–Fixman–Burchard equation containing two additional parameters. Such a relation, covering the entire domain of molecular weights, is necessary because for high expansion coefficients not only the Stockmayer–Fixman–Burchard (SFB) equation is inadequate[4,5], but even the proposed modified SFB relation[2], containing only one additional parameter, does not give an acceptable linear representation.

From reference 2 we take the equation:

$$\left(\frac{1}{[\eta]_\Theta} - \frac{1}{[\eta]}\right) M^{1/2} = A_2(M^{1/2} - DM) + A'$$

and substitute $D - CM$ for D, where C is a new constant. Thus,

$$\left(\frac{1}{[\eta]_\Theta} - \frac{1}{[\eta]}\right) M^{1/2} = A_2(M^{1/2} - DM + CM^2) + A'$$

and instead of the corrected SFB equation:

$$\frac{[\eta]}{M^{1/2}} = \frac{1}{A_1} + \frac{A_2}{A_1^2} M^{1/2}(1 - DM^{1/2}) + \ldots \qquad (1)$$

from reference 2 we obtain finally:

$$\frac{[\eta]}{M^{1/2}} = \frac{1}{A_2} + \frac{A_2}{A_1^2} M^{1/2}(1 - DM^{1/2} + CM^{3/2}) + \ldots \qquad (2)$$

As described in reference 2 the parameter D is given by:

$$D = 12 \times 10^{-4}(a - 0.5) \qquad (3)$$

where a is the exponent of the Mark–Houwink–Sakurada (MHS) equation. Using a large number of experimental results taken mainly from the literature we have attempted to find a value for the constant C, maintaining the same value for D. The best value of C, giving a linear relation over the entire domain of molecular weights when $[\eta]/M^{1/2}$ and $M^{1/2} - DM + CM^2$ are plotted according to the new equation (2), is given by:

$$C = 6 \times 10^{-8} D \qquad (4)$$

as seen from the following examples.

Poly(vinyl acetate)/CHCl$_3$ and poly(vinyl acetate)/acetone

The experimental results for these systems were taken from Ueda and Kajitani[6]. In *Figure 1* we represent these

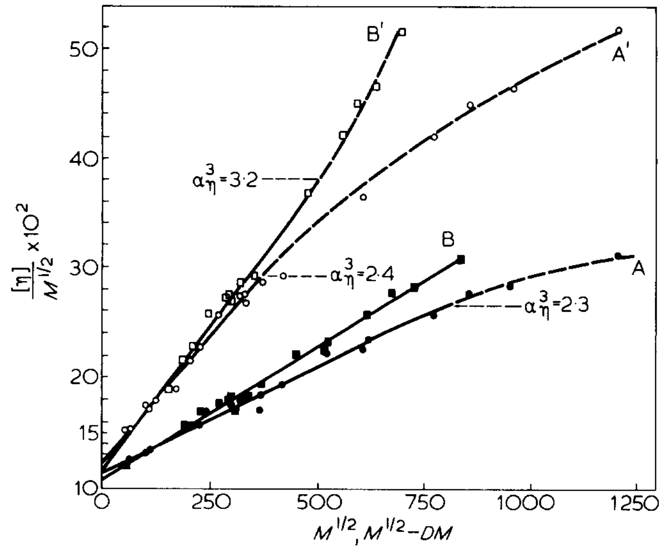

Figure 1 A (●), Plot of $[\eta]/M^{1/2}$, and B (■), *versus* $M^{1/2} - 2.52 \times 10^{-4} M$ for poly(vinyl acetate) samples, in acetone at 6°C. A' (○), plot of $[\eta]/M^{1/2}$ and B' (□) *versus* $M^{1/2} - 3.48 \times 10^{-4} M$ for poly(vinyl acetate) samples in CHCl$_3$ at 6°C. Results from ref 6

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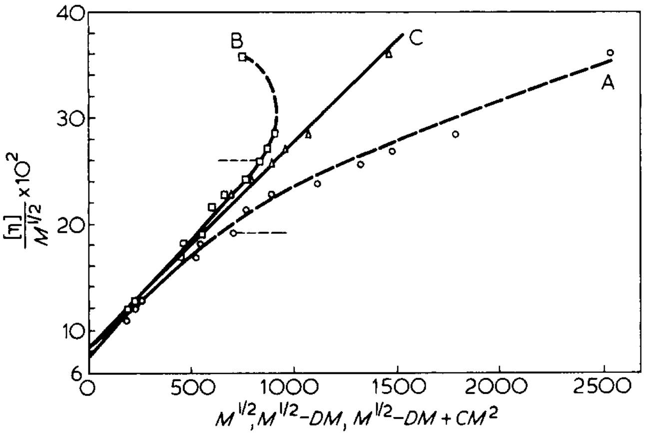

Figure 2 A, plot of $[\eta]/M^{1/2}$ *versus* $M^{1/2}$; B, *versus* $M^{1/2} - 2.76 \times 10^{-4} M$; and C, *versus* $M^{1/2} - 2.76 \times 10^{-4} M + 16.6 \times 10^{-12} M^2$ for PS samples in toluene at 35°C. Results from ref 7

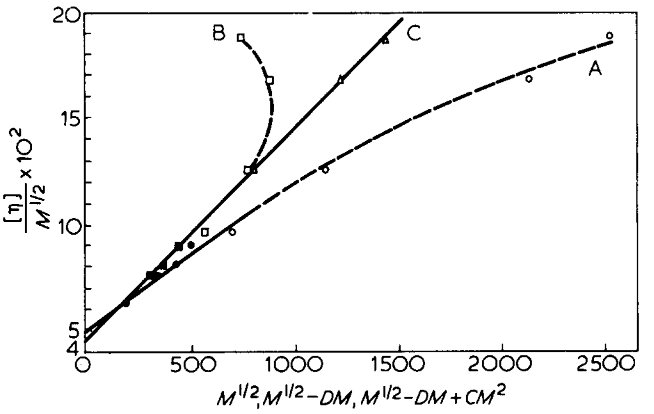

Figure 3 A, Plot of $[\eta]/M^{1/2}$ *versus* $M^{1/2}$; B, *versus* $M^{1/2} - 2.76 \times 10^{-4} M$; and C, *versus* $M^{1/2} - 2.76 \times 10^{-4} M + 16.6 \times 10^{-12} M^2$ for poly(methyl methacrylate) samples in acetone at 25°C. Results from refs 8 and 9 (○, □,△) and this work (●,■)

results according to the SFB equation and equation (1). For both systems a curvature in the SFB representation is observed, beginning at a value of the expansion coefficient α_η^3 of the order of 2.3. In the case of poly(vinyl acetate)/$CHCl_3$ and for an α_η^3 value higher than 3.2 even equation (1) gives a slight curvature. The curves in *Figure 1* clearly show that the equation (2) gives an improved linear relation between $[\eta]$ and M, but is still inadequate in the domain of high values of the expansion coefficients.

Polystyrene/toluene

Using the experimental results of Nakata[7] $[\eta]/M^{1/2}$ is plotted in *Figure 2* as a function of $M^{1/2}$-DM (equation 1) and as a function of $M^{1/2}$-$DM + CM^2$ (equation 2). Equation (2) gives a linear relation over the entire domain of molecular weights. The values D and C are obtained from equations (3) and (4) and taking the exponent a of the MHS equation to be 0.73. In this system, as in the following systems, we use essentially the domain of molecular weights from 10^5 to 10^6: the exponent a can then be found.

Poly(methyl methacrylate)/acetone

The experimental results for this system are taken from Lütze and Meyerhoff[8,9]. In *Figure 3*, as in the preceding system, only the application of equation (2) gives a linear representation of viscosity data as a function of molecular weight for the entire domain of molecular weights.

The non linearity of the SFB equation starts at $\alpha_\eta^3 \sim 2.2$ while the linearity of equation (1) is maintained up to $\alpha_\eta^3 \sim 2.8$.

Amylose acetate/nitromethane

The viscosimetric results for this system were obtained from the article of Banks and Greenwood[10]. *Figure 4* shows that only the application of equation (2) gives a linear rep-

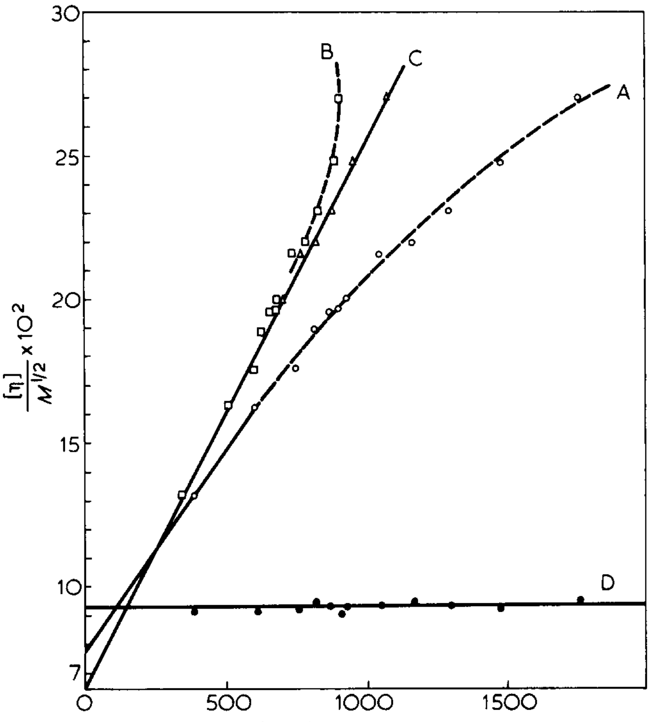

Figure 4 Plot of $[\eta]/M^{1/2}$ *versus* $M^{1/2}$; B, *versus* $M^{1/2} - 2.76 \times 10^{-4} M$; and C, *versus* $M^{1/2} - 2.76 \times 10^{-4} M + 16.6 \times 10^{-12} M^2$ for amylose acetate samples in nitromethane; D, plot of $[\eta]/M^{1/2}$ *versus* $M^{1/2}$ for the same samples in nitromethane/propanol (43.3/56.7) solvent mixture (Θ-solvent). Results from ref 10

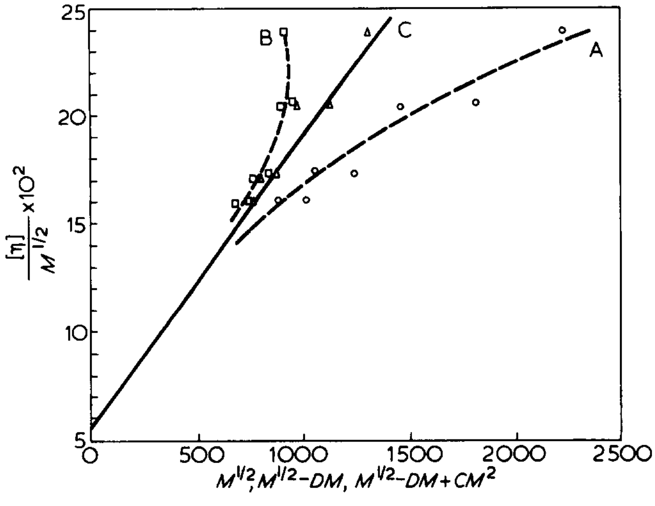

Figure 5 A, Plot of $[\eta]/M^{1/2}$ *versus* $M^{1/2}$ *versus* $M^{1/2}$; B, *versus* $M^{1/2} - 2.64 \times 10^{-4} M$ and C, *versus* $M^{1/2} - 2.64 \times 10^{-4} M + 15.8 \times 10^{-12} M^2$ for poly(ethyl methacrylate) samples in toluene at 35°C. Results from ref 13

resentation over the entire domain of molecular weights (curve C). The value of a in the MHS relation is 0.73 and we obtain $D = 2.76 \times 10^{-4}$ (equation 3) and $C = 16.6 \times 10^{-12}$ (equation 4). Equation (1) gives a linear representation up to $\alpha_\eta^3 \sim 3.2$, (curve B), while the SFB equation has an upper limit $\alpha_\eta^3 \sim 2.4$ (curve A).

The extrapolation of curve C gives a value of K_Θ equal to 6.5×10^{-2} cm^3 g^{-1}. This value is lower than the value obtained in the solvent mixture nitromethane/propanol[10] (curve D). This difference can be explained on the basis of the thermodynamic properties of the binary solvent mixtures[11]. The value of K_Θ obtained for pure nitromethane approaches that obtained by Cowie and Toporowski[12].

Poly(ethyl methacrylate)/toluene

For this system we used only polymer samples of high molecular weight[13] and application of the SFB equation (*Figure 5*) gives an ambiguous extrapolation ($K_\Theta = 10.69 \times 10^{-2}$)[13]. The application of equation (2) not only gives a linear representation between $[\eta]$ and M but extrapolation to $M = 0$ also gives a correct K_Θ value ($K_\Theta = 5.5 \times 10^{-2}$, *Figure 5*). A similar K_Θ value is obtained for the same polymer in a Θ solvent[13] or using the Flory–Fox plot[14] when the polymer is dissolved in a good solvent[13].

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Interaction of water with some epoxide adhesives

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The effect of water on the epoxides is generally an undesirable one: adhesive joints suffer a decrease in strength, sealants transmit water to components such as microprocessors which they are meant to protect, and matrix resins may suffer loss of stiffness by plasticization.

Several factors may be involved in these unwanted processes. These may include: the rate of diffusion of water and the solubility of water in the epoxide; modification of mechanical properties by water ingress, which in some cases may involve the material passing from the glassy to leathery state; and the effect of water on interfaces, be they fibre–matrix, adhesive–adherend, or sealant–substrate.

We have attempted to examine some of these factors, namely solubility, diffusion coefficient, and depression of glass transition temperature for a series of epoxides. Six commonly used epoxides were chosen for this work, and from the start it was intended to choose later one of these for a more detailed study which would include the use of the chosen adhesive in durability trials on bonded metal joints. This work has been completed[1] and will be published later. The simple experimental method was based on following mass uptake of water by weighing on a laboratory balance.

EXPERIMENTAL

A commercial liquid resin consisting largely of the diglycidyl ether of bisphenol A, having an epoxide molar mass in the range 182–194 was used. It was employed with the six hardeners which are recorded with their formulations and conditions of cure in *Table 1*, the information being taken from the sources quoted and so typical of the current use of these materials. With the exception of TETA which is hygrocopic and which was distilled at reduced pressure from over calcium hydride, all materials were used as supplied.

Adhesive films were prepared by a modified version of a method described by Perera and Heertjes[8] for the preparation of paint films. Tin foil (0.13 mm thick) was rollered to a smooth finish on a wet glass plate using a rubber roller. Adhesive was spread onto the tin foil using a thin layer chromatography spreader. After cure, the tin foil was removed by peeling. The tin foil (from Hopkin and Williams Ltd.) was used as supplied. It seems very likely that its successful use for this purpose depended on it being covered with a layer of rolling oil. To assist spreading, the adhesive was applied whilst hot onto a surface which had been preheated in an overn.

Cured films were cut into samples approximately 20 mm x 20 mm, and the thickness of each sample was measured in at least 5 places with a micrometer. Typically the samples were (350 ± 17) μm thick.

The sorption of liquid water was investigated. Film samples were placed in individual 50 g screw-capped jars containing distilled water. Some jars were kept in a water bath maintained at 25 ± 0.5°C and others in an oven at either 45 ± 0.8°C or 70 ± 1°C. Films were removed periodically, dried with filter paper, weighed, and then returned. The sorption process was followed in this manner until equilibrium was reached, which was usually after 2 to 4 months.

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