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On macro- and microviscosity of high polymer solutions

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(*Received* 1 *July* 1980)

The diffusion coefficient, D, in the liquid phase is related to the liquid viscosity η by the Stokes–Einstein equation:

$$D = \frac{RT}{6\pi r \eta} \qquad (1)$$

where r is the radius of diffusant molecule. So D may be used as a measure of the viscosity coefficient of the liquid media.

The high viscosity of the polymer solutions is due to the network formed by long chain molecules which contains a large amount of pure solvent in each cell. Viscosity depends both on the polymer molecular mass and the concentration. But the solvent properties in these cells depend only on the cell size, which is a function of the polymer weight concentration, and would be independent of the molecular mass of the polymer if the chain lengths were large enough to be compared with the cell size.

The difference between the measured viscosity of a high polymer solution and its microviscosity which affects molecular mobility within it has previously been reported[1,2].

The dependence of the diffusion coefficient of the low molecular mass compounds on the concentration of polystyrene in ethylbenzene, which is a low molecular mass model of the polymer monomeric unit, has been studied. Our aim was to verify the assumption that the polymer solution microviscosity is independent of the molecular mass of the dissolved polymer.

EXPERIMENTAL

The macroviscosity of concentrated polymer solutions were measured by the thick layer method[3,4], recording the reduction of the mild β-radiation intensity I caused by penetration of the labelled compound into the substance studied. As low-molecular mass probe compounds 2,6-di-tert-butyl-4-methyl phenol and 2,2'-methylene-bis(4-methyl-6-tert-butyl phenol), labelled with ^{14}C were used. All experiments were conducted at 20 C.

RESULTS AND DISCUSSION

According to the theory of ref 3, the radiation intensity–time curves expressed as I/I_0 vs. $t^{-1/2}$ possessed as asymptote passing through the coordinate origin (*Figure 1*). The asymptote slope, m, is related to the diffusion coefficient by:
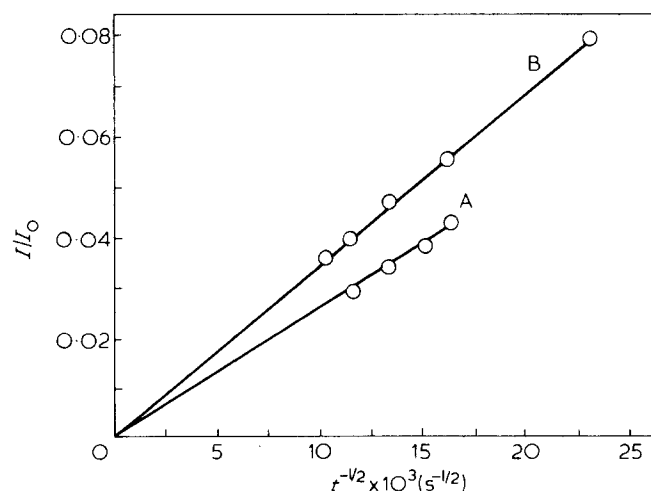

Figure 1   Change in radiation intensity in the course of diffusion of 2,6-di-tert-butyl-4-methylphenol (A) and 2,2-methylene-bis(4-methyl-6-tert-butylphenol) (B) in 40% polystyrene solution. Temperature, 20° C
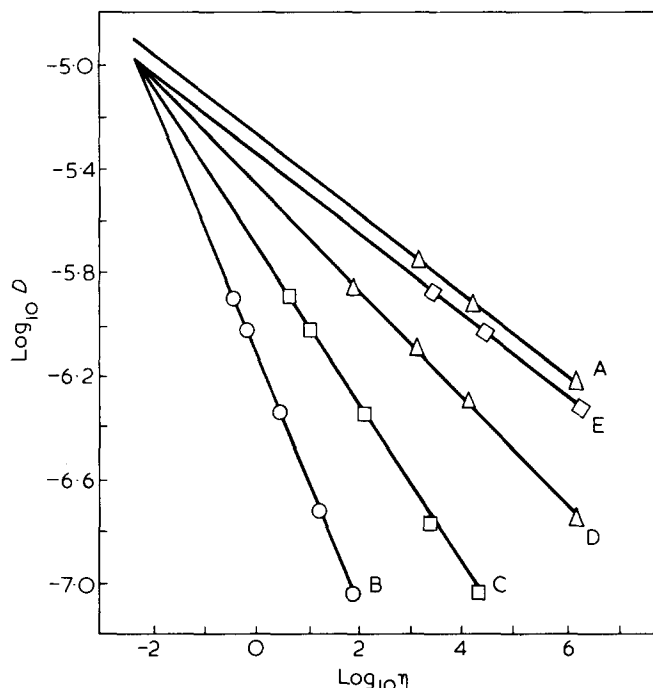
Figure 2 Logarithm of diffusion coefficient as a function of solution viscosity for 2,6-di-tert-butyl-4-methylphenol) (A) and 2,2-methylene-bis(4-methyl-6-tert-butylphenol) (B—E). Molecular mass of polystyrene: B, 5.5×10^4; C, 1.16×10^5; A and D, 1.08×10^6; and E, 3.0×10^6

Figure 3 Dependence of $\log_{10} D$ on polystyrene concentration: 2,6-di-tert-butyl-4-methylphenol (A) and 2,2-methylene-bis(4-methyl-6-tert-butylphenol) (B). Molecular mass of dissolved polymer: $\bigcirc$, 5.5×10^4; $\square$, 1.16×10^5; $\triangle$, 1.08×10^6 and $\Diamond$, 3.0×10^6

$$D = \frac{1}{\pi \mu^2 m^2} \qquad (2)$$

Here μ is the coefficient of radiation absorption.

Figure 2 shows the diffusion coefficients as functions of the solution viscosity. The curves for each molecular mass are seen to be straight lines in coordinates $\log D$ vs. $\log \eta$. The lines for the same probe compound intersect at one point, corresponding to the pure solvent viscosity (6.65 poise). This permits the evaluation of D for ethylbenzene. D cannot be directly measured by the method developed for solids or for high viscosity liquids.

As expected, the diffusion coefficient of each probe compound appears to be an unambiguous function of the polymer concentration and for the given concentration does not depend on the molecular mass of polystyrene in the range 5.5×10^4–3.0×10^6 (*Figure 3*).

We have calculated values of the microviscosity coefficient using the Stokes–Einstein equation and assuming that in a pure solvent both macro- and microviscosity values are the same. The results are shown in *Figure 4*, where two different curves were obtained for microviscosity vs. polymer concentration, using two different compounds as probes.

The macromolecular network is inhomogenous, and the sizes of its cells are comparable with those of the solvent and diffusant molecules. The greater the size of the diffusing molecule, the fewer the number of cells through which it can pass. This is why 'microviscosity', calculated formally by the Stokes–Einstein equation, depends on the nature of the probe molecule used in its evaluation.

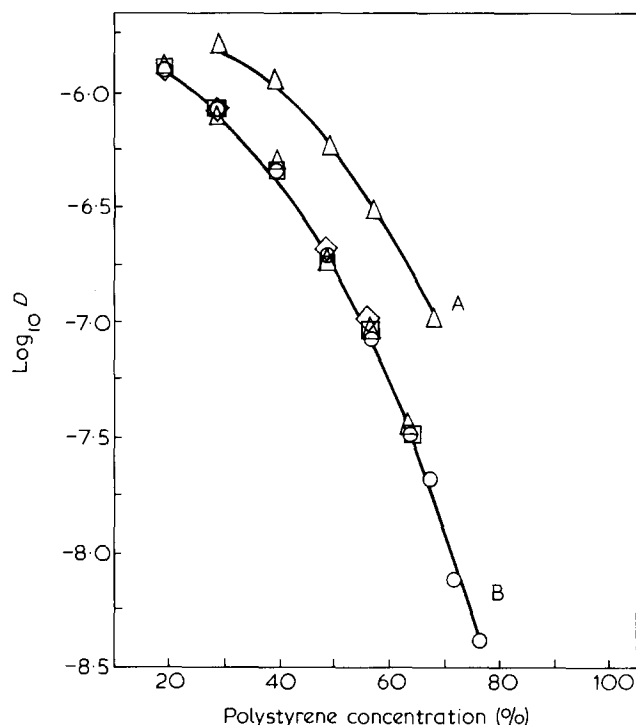Thus, the notion of microviscosity seems to have no definite meaning for concentrated polymer solutions.

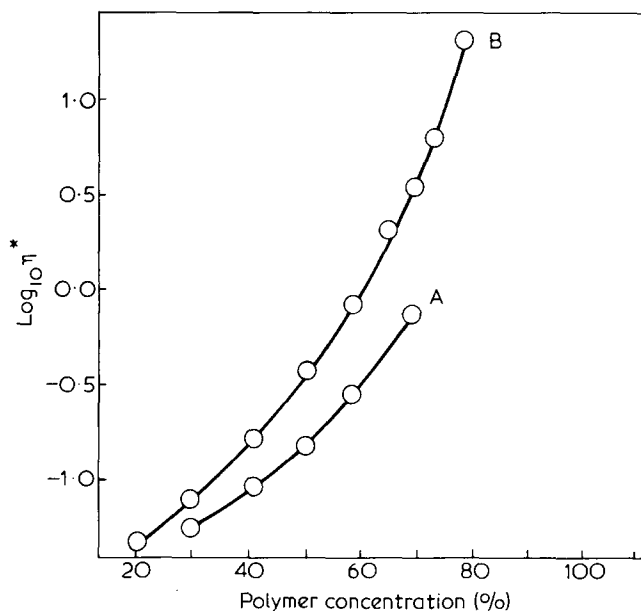*Figure 4* 'Microviscosity' values measured using probes A, 2,6-di-tert-butyl-4-methylphenol; and B, 2,2-methylene-bis(4-methyl-6-tert-butylphenol)

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