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## Light Scattering and Dynamics of Flexible Polymers [Abstract Only and Discussion]

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## Light scattering and dynamics of flexible polymers [abstract only]

BY P. G. DE GENNES

The paper reviewed some salient dynamic properties of entangled polymer solutions and of gels: sedimentation and cooperative diffusion. The photon beat experiments of Adam & Delsanti (on solutions) and of Candau *et al.* (on gels) were described together with the corresponding dynamic scaling laws.

*Discussion*

A. J. HYDE (*Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K.*). De Gennes has made reference to measurements by Adam & Delsanti on a very high molecular weight ( $24 \times 10^6$ ) polystyrene in a good solvent, and these results have been compared with a previously derived scaling law. While there is no reasonable doubt that the values of the correlation coefficient or line broadening at low  $kR$  values (low angles) are related in some way to translational diffusion, and at high  $kR$  values to internal chain modes, difficulties of interpretation may arise at the high concentrations used. If one calculates, by using Adam & Delsanti's own radius-of-gyration data, the total volume occupied by the polymer molecules per unit volume of solution at their lowest experimental concentration, it is considerably greater than unity. The polymer coils, of course, contract from their expanded 'good solvent' size so as to fit into the available volume, but the extent of contraction is unknown since conventional light scattering cannot measure the radius of gyration at finite concentration. The lower limit of contraction is known to be approximately the ' $\theta$ ' solvent dimension, but this will only occur at much higher concentrations (*ca.* eight times that being considered). The polymer coils are thus in an unknown constrained state, possibly approximating a 'close-packed sphere' condition. Under such conditions it is clear that translational diffusion will be markedly hindered and the internal motions will not be those of an unrestricted polymer molecule in a good solvent. To get values for essentially independent molecules it would seem to be necessary to work, not at concentrations less than  $c^* = M/s^3$  ( $M$  = molecular mass,  $s$  = r.m.s. radius of gyration, Å), the concentration for existence of entanglements (the criterion used by Adam & Delsanti), but at concentrations much less than that corresponding to a close-packed system of spheres of diameter roughly equal to the r.m.s. end-to-end distance of the polymer molecule in a good solvent; the latter concentration would be about one eighth of  $c^*$ .

P. G. DE GENNES. Our answer to Dr Hyde's question is based on the experimental relaxation time as a function of concentration for high  $kR$  values:

$$\begin{aligned} c &= 5.5 \times 10^{-4} \text{ g/g}, c/c^* = 0.5, \tau^{-1} = 2.9 \times 10^3 \text{ s}^{-1} (kR = 8), \\ c &= 1.67 \times 10^{-4} \text{ g/g}, c/c^* = 0.17, \tau^{-1} = 2.88 \times 10^3 \text{ s}^{-1} (kR = 8), \\ c &= 6.17 \times 10^{-5} \text{ g/g}, c/c^* = 0.06, \tau^{-1} = 3.05 \times 10^3 \text{ s}^{-1} (kR = 8), \end{aligned}$$

the mean value of  $\tau^{-1}$  is  $2.96 \times 10^3 \text{ s}^{-1}$  and the precision is about  $3 \times 10^{-2}$ .

Thus for high values of  $kR$ , we measure the same characteristic time when  $c$  varies in such a way that  $\frac{1}{20} < c/c^* < \frac{1}{2}$ .

There are no visible concentration effects in this range.

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