Carbohydrate Polymers **2 (1982) 238–241**

ORIENTATIONAL ORDER IN MESOMORPHIC CELLULOSE SOLUTIONS

P. SIXOU, S. DAYAN, G. M. GILLI, F. FRIED, P. MAISSA, M. J. VELLUTINI & A. TEN BOSCH

Laboratoire de Physique de la Matière Condensée, Université de Nice, 06034 Nice Cedex, France

In this paper some studies on mesomorphic solutions of cellulose derivatives are presented.

Such systems are of interest at a fundamental level because they are not well understood. They are also of technological interest because a major problem is the improvement of the mechanical properties of fibres, films and composites. These mechanical properties can only be obtained because the polymeric solutions are in a liquid crystalline state, i.e. mesomorphic above a critical concentration and therefore the macromolecules have a natural tendency to align. This approximates to precrystallisation which facilitates chain extension and decreases entanglements.

Two essential problems to be solved are a fine characterisation of the mesomorphic order and an understanding of the mechanisms which lead to orientational order.

To resolve these questions the following systematic approach has been adopted:

Firstly it is deemed necessary to show that the solution is mesomorphic. Several methods can be employed to do this:

(i) Microscopy between crossed polarisers: if the solution is anisotropic a characteristic pattern is seen (Navard *et al.*, 1981).
(ii) Viscosity of the solution: a peak of viscosity as a function of concentration is observed (Dayan *et al.*, 1982*b,c*) (Fig. 1).
(iii) Differential scanning calorimetry (Dayan *et al.*, 1982*c*; Dayan *et al.*, 1982*b*): a peak is observed, the enthalpy of the transition is small (Navard *et al.*, 1981).

The second step is to determine how this property depends on the solvent and chain characteristics. The effect of DP, solvent and degree and nature of substitution have been studied in the case of different cellulosic derivatives (Dayan *et al.*, 1982*c*; Gilli *et al.*, 1982).

The third step is to establish if the phase is nematic, as in some aromatic polyamide solutions, or if this phase is cholesteric, as in some polypeptide solutions. Circular

Carbohydrate Polymers 0144-8617/82/0002-0238/$02.75 – © Applied Science Publishers Ltd, England, 1982
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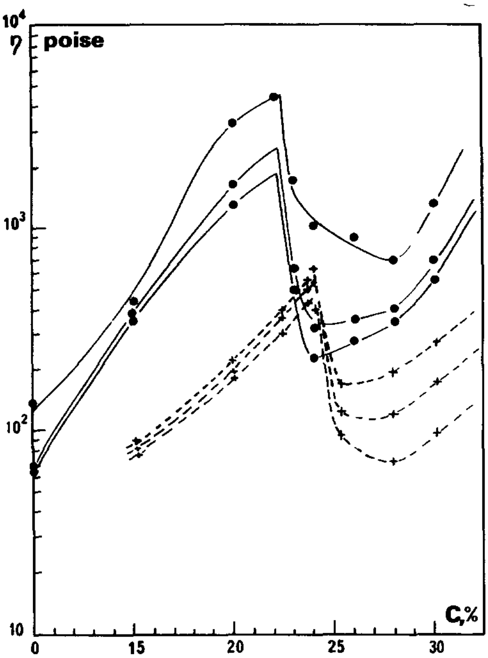

Fig. 1. Viscosity plotted against concentration for solutions of two different molecular weight fractions of cellulose acetate in trifluoroacetic acid; temperature, −20°C. Numbers show the shear rates at which the measurements were made. (The same shear rates were used for the lower molecular weight fraction.) ●, $M_W = 56\,000$; x, $M_W = 30\,300$.

dichroïsm measurements were made in the vicinity and on either side of the phase transition. In the anisotropic solution, a strong peak is observed around 650 or 700 nm. The peak increases with temperature (Fig. 2). Circular dichroïsm due to an addition of a small amount of an achiral dye to the solution was also studied (Lematre *et al.*, 1982).

The fourth step is to predict for given chain and solvent properties where the anisotropic phase will appear. This prediction requires a preliminary determination of chain rigidity. Two models are available, those of Kratky & Porod (1949) and Yamakawa & Fujii (1974). In the latter, both the diameter of the chain and its persistence length are taken into account. In several cases the hydrodynamic diameter and persistence length can be determined from a knowledge of the intrinsic viscosity as a function of molecular weight (Dayan *et al.*, 1982*d*).

The experimental phase diagrams (Navard *et al.*, 1981; Dayan *et al.*, 1982*c*) agree qualitatively with the Flory theory (Flory, 1956*a*,*b*) but for quantitative predictions it is necessary to take into account a change of conformation of macromolecules with concentration. This was obtained from the Pincus-de Gennes theory (Pincus & de Gennes, 1978).

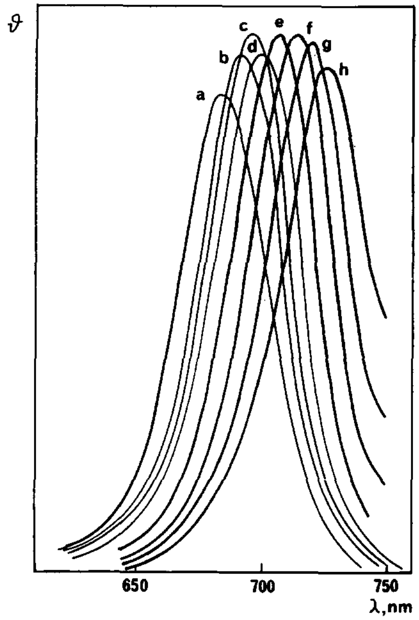

Fig. 2. Circular dichroïsm peaks at different temperatures for a cellulose acetate/trifluoroacetic acid solution. $M_W = 56\,000$; cellulose = 27% by wt. a, 35·3°C; b, 36°C; c, 37°C; d, 38°C; e, 39°C; f, 41°C; g, 42°C; h, 43°C.

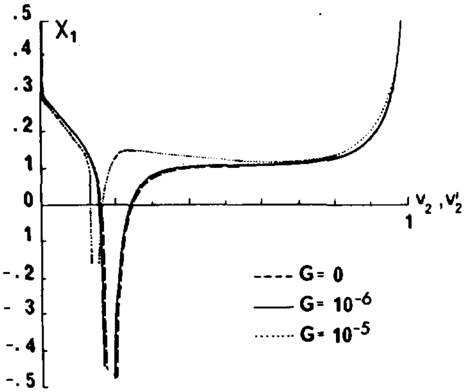

Fig. 3. Modification of the phase diagram due to an elongational flow. G is a non-dimensional parameter defined by:

$$G = \Gamma b^2/(8KT/\xi)$$

where Γ = stretching rate, b = size of the element (monomer), ξ = friction coefficient, T = temperature. X_1 = polymer solvent parameter, v_2 = concentration on first appearance of anisotropic phase, v_2' = concentration when completely anisotropic solution.

The notation is that used by Marrucci & Ciferri (1977).

If the concentration where the phase transition appears is known, two problems must still be resolved. Firstly, how is the transition reached, i.e. what are the pretransitional properties? Secondly, when the transition occurs, what is the degree of order in the solution? The pretransitional regime was studied by quasi-elastic light scattering (Fried *et al.*, 1982) and the post transitional regime by NMR (C^{13} and F splitting and anisotropy of chemical shift) (Dayan *et al.*, 1982*a*).

Last but not the least there remains the problem of flow. The theory of Flory can be extended to show that the anisotropic phase appears at lower concentrations when elongational flow is applied (Fig. 3).

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