polymer communications

Refractometry of cellulose triacetate solutions

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Measurements of refractive index are presented for the liquid crystal-forming polymer cellulose triacetate dissolved in trifluoroacetic acid. The refractive index increment changes above the critical concentration to a lower value. This change is ascribed to the light scattering caused by orientation fluctuations in the alignment vector of the molecular axes.

Keywords Refractometry; liquid crystal polymer; cellulose triacetate; mesophase; refractive index; liquid crystal

Introduction

Cellulose acetates dissolved in trifluoroacetic acid (TFA) are known to develop a lyotropic liquid crystalline order above a certain critical concentration c_1^{**}[1,2,3]. The order is generally thought to be cholesteric. We report here the use of refractometry as a novel determination of the critical concentration and discuss theories of liquid crystal formation.

Experimental

Solutions of cellulose triacetate (CTA) in TFA were prepared at room temperature by prolonged mixing. The polymer ($72\,000 < M_w < 74\,000$, degree of substitution 2.9) and the TFA were used as received from Fluda A. G. Polymer concentrations are given in g of dry polymer per ml of solvent. Refractive indices were measured at a wavelength of 589 nm using a precision Abbé refractometer (Bellingham and Stanley Ltd). This was a critical angle measuring instrument.

Results and Discussion

Figure 1 shows the refractive index n' of solutions plotted with polymer concentration c. The refractive index increment $\frac{dn'}{dc}$ is constant at 0.185 ml g^{-1} up to the critical concentration c_1^{**} and 0.09 ml g^{-1} thereafter for the anisotropic solutions. A clear change in $\frac{dn'}{dc}$ is apparent at a polymer concentration of 0.34 g ml^{-1}. This agrees exactly with c_1^{**} determined by many other method.

Values of $\frac{dn'}{dc}$ close to the measured value of 0.185 ml g^{-1} were calculated using the Gladstone–Dale or Lorentz–Lorenz relations, with the refractive indices and densities of the two pure components. An explanation for the abnormally low value of 0.09 ml g^{-1} was therefore sought.

The Abbé refractometer measures the critical angle of light rays which have travelled almost parallel to the prism refracting surface in a thin layer of solution. Weak forces near and from glass surfaces are well known to preferentially orientate liquid crystalline phases. A cholesteric structure consists of planes where molecular axes have a common direction $\vec{n}$. These planes are arranged in a helical manner along the pitch vector $\vec{N}$. If preferential order were present due to the glass surface we would expect $\vec{n}$ to be either parallel or perpendicular to the prism refracting surface. The perpendicular orientation cannot coexist with a cholesteric structure. The parallel orientation of $\vec{n}$ to the prism surface could coexist with a cholesteric structure. However, no special treatment was given to the prism refracting surface, so that from one sample to another $\vec{n}$ would be expected to take up random orientations in the plane of the refracting surface. If this had occurred, the measured value of n' would have fluctuated from sample to sample between the values n'_0 and n'_e, these being the ordinary and extraordinary refractive indices, respectively, of the

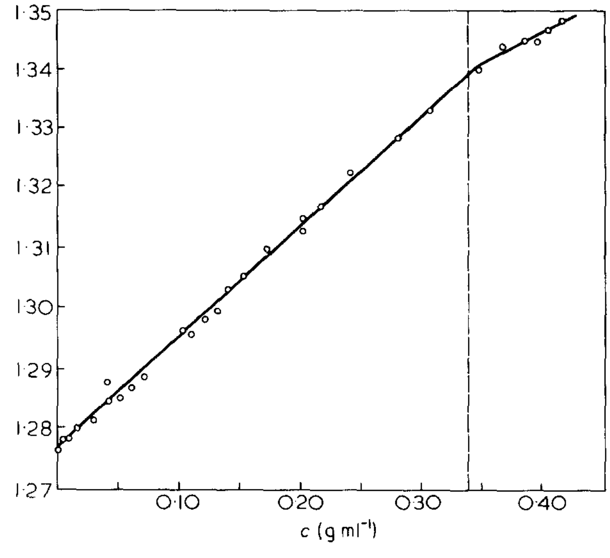

Figure 1 Refractive index n' at 589 nm plotted with concentration c of polymer for cellulose triacetate/trifluoroacetic acid solutions. The vertical broken line marks the concentration (0.34 g ml^{-1}) above which the solutions were in the liquid crystalline state

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mesophase. From *Figure 1*, it is evident that the experimental scatter in n' was of the order of 0.002, about 35 times smaller than $n'_0 - n'_e$ values typical of liquid crystalline phases, e.g. $|n'_0 - n'_e| \simeq 0.07$ reported for cellulose[4]. Any orientation for $\vec{n}$ close to the refracting surface therefore does not explain the change of $\frac{dn'}{dc}$ at c_1** in *Figure 1*.

Another possibility is that the glass prism induced a cholesteric–nematic phase transition near its surface and that $\vec{n}$ was orientated normally to the surface, i.e. a homeotropic state. This kind of transition, without the aid of an externally applied field, has never been reported and we regard it as unlikely that weak surface forces could induce such a phase change.

The explanation which we favour is as follows. The solutions became turbid above c_1**. This is usually ascribed to spontaneous fluctuation of the alignment $\vec{n}$, the alignment having a mean coherence length ρ[5]. The theory of refraction in scattering media shows that the effect of scattering by discrete objects can decrease the refractive index of the medium, depending on the size of the scattering object[6]. E.g., it can be shown[6] that $\frac{dn'}{dc}$ of a dispersion of spheres decreases rapidly with increasing sphere diameter, for diameters exceeding about 1 μm. Thus, the fluctuations of $\vec{n}$ in regions of mean size ρ probably accounts for the difference in $\frac{dn'}{dc}$ below and above c_1**.

It is of interest to consider the Flory[7] and Pincus–De Gennes[8] theories of lyotropic liquid crystal formation in the light of our results and conclusions. The Flory theory predicts the ordering of semiflexible or rigid macromolecules as their concentration increases. The ordering begins at a concentration c_1** and continues until the fully ordered phase is reached at c_2**. The interval $c_1^{**} < c < c_2^{**}$ is biphasic, i.e. a coexistence of isotropic and liquid crystalline phases is predicted. The Pincus–De Gennes theory predicts an isotropic liquid crystalline transition at c_1** with no biphasic interval. On the basis of refraction theory as discussed above for scattering media, $\frac{dn'}{dc}$ would not be constant in the biphasic region as the regions of the liquid crystalline phase increased in size. The constant value of $\frac{dn'}{dc}$ observed above 0.34 g ml^{-1} could be explained on the Flory theory by assuming that c_1*–c_2* was too small to detect. A more likely explanation is that the formation of liquid crystals in the CTA/TFA system is described by the Pincus De Gennes theory. This theory explains qualitatively our results with no further assumption than the fluctuations of alignment $\vec{n}$ over regions similar to, or larger in size than the optical wavelength. Considerable independent experimental evidence exists for these fluctuations in the liquid crystal phase of CTA/TFA[9].

Note added in proof

We have noted the paper of Tseng *et al.* (Macromolecules, 1980, **14**, 715). Using acetoxypropyl cellulose, these workers have measured the refractive index below and above the critical concentration. Although their data also shows a change in the refractive index increment at the critical concentration, it is smaller than we found and not discussed by the authors. Above the critical concentration Tseng *et al.* found a spontaneous birefringence which we did not observe.

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Microheterogeneous structure of liquid crystalline polymers

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Liquid crystalline polymers with phenyl benzoate side groups with various lengths of flexible chain-end were synthesized. Small-angle X-ray scattering studies were carried out. Layer structures in the liquid crystalline polymers were characterized and the microheterogeneous structure was investigated. It was concluded that the microstructure is dependent on the length of the flexible mesogenic chain-end.

Keywords Structure; polymers; liquid crystalline; microstructure; chain-end; mesogenic; small-angle X-ray scattering

Liquid crystalline (LC) polymers exhibit both the properties of liquid crystals and the traditional advantages of polymeric materials, while behaving as a new class of macromolecular systems, being models of 'ordered' amorphous polymers or 'disordered' crystalline polymers.

Studies of short-range order in LC polymers resulted in certain relationships governing structure formation[1]. Data on the microphase structure of the polymers are few, even though it is this structure which determines the LC properties.

Electron-microscope studies on cholesterol-containing

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