Gel formation and liquid crystalline order in cellulose triacetate solutions*

G. H. Meeten and P. Navard*

Department of Physics, Sir John Cass School of Science and Technology, City of London Polytechnic, 31 Jewry Street, London EC3N 2EY, UK

The formation of a liquid crystalline state of cellulose triacetate solution in trifluoroacetic acid was studied using optical microscopy, polarimetry and circular dichroism measurements. Below a critical concentration of 34 g/100 ml a clear isotropic solution was formed. Solutions more concentrated than this were in the cholesteric liquid crystalline state. If water was added to the solution, a gel phase was formed if the polymer concentration was above a critical value. We interpret our observations in terms of the Pincus–de Gennes theory and show that the formation of liquid crystalline order involves both inter- and intramolecular forces.

Keywords Liquid crystal polymer; liquid crystal gel; polymer gel; anisotropic gel; cellulose polymer solution; polymer liquid crystal

INTRODUCTION

Anisotropic polymer solutions appear to fall into two classes. Those of the first category behave largely as predicted by Onsager[1] and Flory[2,3] and consist of rigid or semi-rigid polymers. Aromatic polyamides[4,5], polyisocyanates[6] and some polypeptides[7] are examples. A characteristic property predicted by the above theories is the existence of a range of polymer concentration, where the isotropic and anisotropic phases coexist.

For anisotropic polymer solutions in the second category no distinct biphasic region occurs; as the polymer concentration is increased, the whole sample changes from an isotropic to the fully anisotropic state. Cellulose[8], its derivatives such as hydroxypropylcellulose in water[9] or other solvents[10], and some polypeptide solutions[11,12], are systems which have been reported to show this. An explanation for this behaviour has been proposed by Pincus and de Gennes[13]. According to their theory, polymer solutions in dilute solutions exist as flexible random coils, and the isotropic-to-anisotropic transition is accomapnied by a coil-to-helix conformation change.

Here we describe our investigation of the isotropic and liquid crystalline states of cellulose triacetate (CTA) dissolved in trifluoroacetic acid (TFA) and of the gel formed when water is added to these solutions. Although we are aware of other studies of liquid crystalline solutions of cellulose derivatives[8–10,14–24] and cellulose acetate systems[19–24], no clear evidence about the molecular conformation in the isotropic and liquid crystalline states in these systems currently exists.

EXPERIMENTAL

Materials

Cellulose triacetate (CTA), $72000 < M_w < 74000$, degree of substitution ~ 2.9, wss obtained from Fluka AG. Trifluoroacetic acid (TFA) (Fluka AG), was used without further purification. The polymer was dried for 12 h at 100°C before dissolution, which was performed by shaking and occasional stirring of the solvent and polymer at room temperature. The time required depended on the concentration and was typically 1 to 4 h. Bubbles were removed from the viscous solutions by centrifuging for about 30 min at 500g.

Polymer concentrations c are quoted as grams of dry polymer per 100 ml of solvent, where the solvent may be pure or a mixed solvent, e.g. TFA/water. The composition of the mixed solvent is quoted as a volume of one component per 100 volumes of mixed solvent. The polymer solutions had only one isotropic-to-anisotropic transition which occurred at a critical concentration denoted by c^{**}.

Techniques

Optical microscopy was performed with a Leitz microscope equipped with a Mettler programmable hot stage and the usual polarization accessories. Most measurements were made using crossed polarizers.

Optical rotation was measured at a wavelength of 546 nm with a Bendix NPL polarimeter, type 143. Pathlengths between 0.1 and 20 mm were used. Circular dichroism measurements were made with a Jasco J-40cs Recording Spectrophotometer, with 50 μm or 10 μm Helma cells.

Terminology

We shall discuss the results in the terminology usually used in liquid crystal studies. Thus if a solution is described as isotropic this is taken to mean that it does not appear birefringent when viewed between crossed polarizers. Strictly speaking, those phases which will be called isotropic solutions in this paper are anisotropic, in
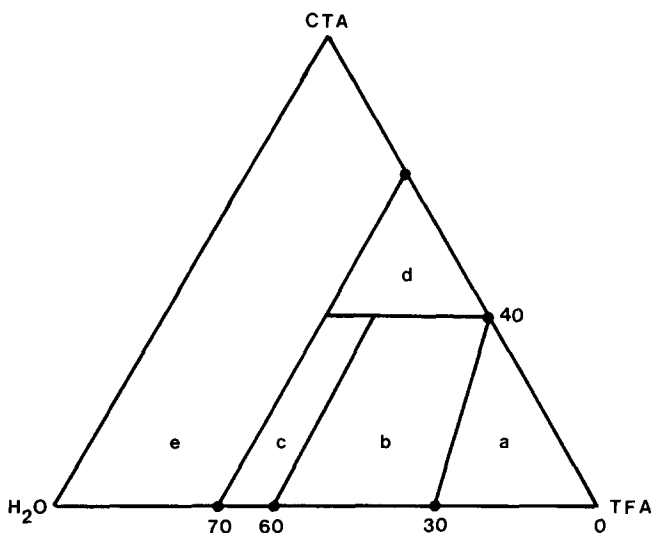
Figure 1 CTA/TFA/water schematic phase diagram at room temperature: a, isotropic, transparent solution; b, isotropic, transparent gel, showing syneresis; c, cloudy gel; d, birefringent transparent gel; e, undissolved CTA (two-phase system)

the sense that they are optically active and therefore possess a different refractive index for right-handed and left-handed circularly polarized light.

RESULTS

Physical appearance and properties of the solutions

Isotropic solutions of CTA/TFA were transparent. At a polymer concentration above 34 g/100 ml, the solutions became turbid, were birefringent when viewed between crossed polarizers and showed iridescent colours when viewed using white light. These are characteristic properties of the cholesteric phase.

Pure water will not dissolve CTA. When mixed with TFA, the mixed solvent behaved in a complex way. The CTA/TFA/water mixture could be in four different states, depending on the relative amounts of the components:

(a) An isotropic and transparent solution when the CTA concentration was less than about 30 to 40 g/100 ml and the concentration of water in the solvent was less than about 30%.

(b) An isotropic, transparent gel when the water concentration exceeded about 30%. The gel showed syneresis, a tendency to contract with expulsion of the solvent after prolonged standing.

(c) A two-phase system, with undissolved CTA and mixed solvent, when the water concentration exceeded about 70%.

Figure 1 shows a schematic phase diagram of the system described above. Gel formation was reversible. If further TFA was added to a gel (40 g/100 ml polymer, 50% water) and allowed to stand for a day it became a solution (20 g/100 ml polymer, 25% water) of similar appearance and about the same magnitude and sign of specific rotation as a freshly prepared solution of the same concentration.

Optical microscopy

Below a polymer concentration of 34 g/100 ml, CTA/TFA solutions did not show any birefringence when viewed between crossed polarizers. More concentrated solutions appeared birefringent. The onset of turbidity and iridescence when viewed in white light coincided with

the appearance of the birefringence when viewed between crossed polarizers. No biphasic region was found and the microscopic appearance of the solution did not change noticeably between 34 and 45 g/100 ml (Figure 2), the latter being the largest concentration used.

Some CTA/TFA/water solutions formed birefringent gels as shown in Figure 3. The bulk of the gel appeared to be birefringent. The samples were prepared by leaving CTA in a container with a TFA/water solution for several days without shaking. When the gel was heated its birefringence increased from 85° to 100°C and levelled off at a constant value of about 120°C. After this treatment the gel retained its crystalline appearance when removed from the hot stage. We surmise that near 85°C the TFA evaporates (boiling point $\sim 73°C$). This is subsequently followed by the water, leaving an anisotropic crystalline sample of CTA.

POLARIMETRY

Optical rotation

The optical rotation of the CTA/TFA solutions was measured as a function of polymer concentration c in the isotropic region, i.e. $c < 34$ g/100 ml.

The specific rotation $[\alpha]$ is proportional to the difference between the indices of refraction for left and right circularly polarized light. It is quoted here as conventionally defined, i.e.
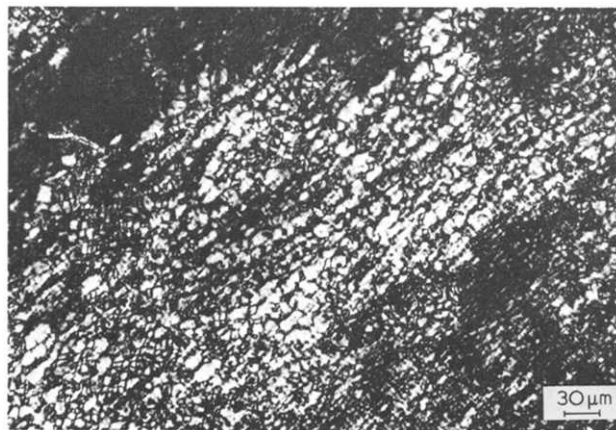

Figure 2 Photomicrograph of a 0.4 g ml⁻¹ CTA/TFA anisotropic solution obtained using crossed polarizers

Figure 3 Photomicrograph of a 0.4 g ml⁻¹ CTA/TFA/water anisotropic gel, with 60% water, 40% TFA, obtained using crossed polarizers. The white lines originate from cutting of the gel and are localized at the surface
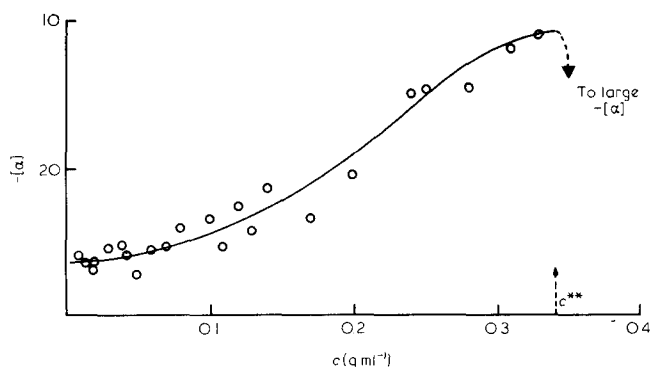
Figure 4 Specific rotation [α] plotted against polymer (CTA) concentration for isotropic CTA/TFA solutions

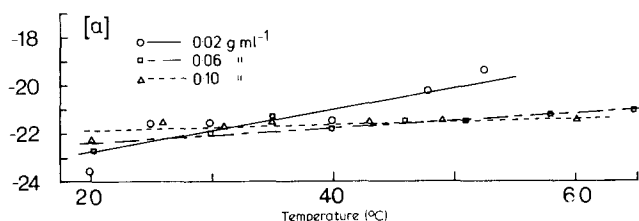Figure 5 Specific rotation [α] plotted against temperature for isotropic CTA/TFA solutions

$$[\alpha] = \frac{100(\alpha - \alpha_0)}{c}$$

where α and α_0 are the optical rotations (in degrees) of the solution and solvent respectively, for a 1 dm pathlength, and c is the concentration as previously defined.

As shown in Figure 4, the magnitude of [α] decreases as the concentration increases until the critical concentration is reached. For the anisotropic phase [α] is about an order of magnitude larger than that of the isotropic phase and is also negative.

Figure 5 shows that [α] has a very small temperature dependence and decreases at higher concentrations. Figure 6 shows the dependence of [α] on the amount of water in the mixed solvent TFA/water. The 40 g/100 ml solution with no water is in the anisotropic cholesteric liquid crystalline state and therefore [α] is large ($\sim 450°C$ g^{-1} ml dm^{-1}) and positive.

Circular dichroism

Circular dichroism spectra were measured for CTA/TFA using 1 g/100 ml solutions. No absorption maxima were found in the wavelength range 220 to 700 nm. A similar result was found for 1 g/100 ml solutions of cellulose acetate dissolved either in dioxan or trifluoroethanol. We conclude for CTA that the optical rotation measured at 546 nm wavelength originates from mechanisms with characteristic wavelengths below 220 nm or above 700 nm. We take this as evidence that [α] originates from the symmetry of the macromolecular chain.

DISCUSSION

Gel formation and specific rotation

Association of macromolecules in solution leading to the formation of gels is a characteristic property of

cellulose acetates and other cellulose derivatives. The most extensively studied example is the gel formed by cellulose acetate dissolved in benzyl alcohol[25,26]. As previously described, the gelation in our case was created by the mixing of cellulose acetate or triacetate with a good solvent (TFA) and a non-solvent (water). In a good solvent polymer–solvent contact is favoured and in a bad solvent polymer–polymer and solvent–solvent contacts are favoured. Hence we surmise that upon decreasing the goodness of the mixed solvent by increasing the proportion of water, the polymer–polymer contact is enhanced and crosslinks form, producing a gel. The reversibility of the gel formation shows that no covalent bonds are involved and the crosslinks formed are probably hydrogen bonds. As shown in Figure 6, the specific rotation [α] of the CTA/TFA/water system changes strongly with solvent composition. We assume that this change is a consequence of the conformation change of the polymer chain. We propose the following explanation for the conformation change. In solid CTA the specific rotation is strongly positive and the conformation exhibits, as do most polysaccharides, a helical secondary structure[27]. In a similar way to the polypeptides, dissolution in a strong acid like TFA destroys the intramolecular hydrogen bonding along the chain as solvent–polymer hydrogen bonds are formed instead[28–38]. This produces less rigid macromolecules. With this less rigid chain is associated a negative specific rotation. This is consistent with the results shown in Figure 6, where adding water (a non-solvent for CTA) is shown to increase the specific rotation of TFA/water/CTA solutions. We suppose that the effect of adding water is to allow the secondary structure to reform. When the water concentration reaches 30% a gel forms and the specific rotation decreases.

We take this to indicate a reduction in the amount of the secondary structure, because the gel is probably formed by intermolecular crosslinking by hydrogen bonds, thus reducing the number of intramolecular hydrogen bonds and hence decreasing the chain flexibility. This supposition is supported by two other results. Figure 6 shows that the effect of the water on the specific rotation becomes stronger as the polymer concentration increases, which indicates that the change in the specific rotation is due to a polymer–solvent interaction. At low concentration of polymer Figure 6
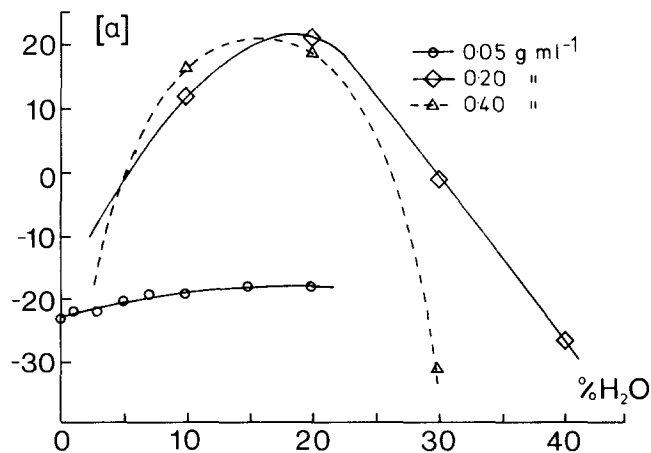

Figure 6 Specific rotation [α] plotted against water concentration for CTA/TFA/water solutions

shows that even at a high water concentration there is still enough TFA for solvating the CTA.

The positive temperature coefficient of $[\alpha]$ found for CTA/TFA shown in *Figure 5* is apparently in disagreement with the above hypotheses. An isolated macromolecular chain would be expected to become less rigid with increasing temperature, and hence according to our supposition that $[\alpha]$ decreases with increasing chain rigidity, a negative temperature coefficient for $[\alpha]$ should result. However, the conformation of some macromolecules in solution is determined by competition between complex inter- and intramolecular forces, each with their own temperature dependence. The results shown in *Figure 5* do not therefore support or contradict our supposition. It is interesting to note, from *Figure 5*, that $d[\alpha]/dt$ would appear to be positive at concentrations greater than about 10 g/100 ml, and this is the region where $[\alpha]$ begins to depend on concentration, as shown in *Figure 4*.

Some of the gels obtained were anisotropic. Cellulose and cellulose derivative gels of this kind have been reported[31,32]. In these cases the anisotropy was explained by the preferential orientation of crosslinked chains in the shear flow caused by mixing the components. In our case, however, the solutions were not stirred, the gel being formed by Brownian diffusion of the molecular species. The origin of the anisotropy in our CTA/TFA/water gels is thus not understood.

Liquid crystal formation

Various experimental methods and theoretical treatments have shown that cellulose and its derivative polymers appear to have fairly inflexible chains with a high kinetic rigidity[33-35]. This rigidity seems to be dependent on both the solvent and the temperature[36] and is probably due to a network of intramolecular hydrogen bonds along the chain. Thus in addition to the usual dependence of a polymer chain conformation on the solvent because of van der Waals and dipolar interactions, there is the possibility of the solvent destroying the intramolecular hydrogen bonds and forming solvent–chain hydrogen bonds instead.

The statistical mechanics of systems of rod-like molecules and of semi-flexible chains was described by Flory[2,3] who predicted a transition to a more densely packed liquid crystalline state above a certain volume fraction. Flory's theory requires x (the axial ratio), the flexibility (fraction f of bent bonds) and the polymer–solvent interaction parameter χ to be specified. There are unfortunately few data for CTA dissolved in TFA which can be used with Flory's theory.

Dayan et al.[37,38] have surveyed the data available in the literature for cellulose derivatives and have compared them to Flory's theory or extensions of it. They conclude that there is good qualitative and semi-quantitative agreement between this theory and experiment. The main problems when comparing experiment with theory appear to be the correct assignment of length to the polymer chain and the estimation of the polymer–solvent interaction parameter. The best fit between experiment and theory was found when the rod length in Flory's theory was taken as the persistence length of the semi-flexible chain. Hence the length of the equivalent rod is much less than the chain contour length. Another problem is the experimental value of the critical concentration c^{**}. For CTA/TFA, Dayan et al.[37] found $c^{**} = 28\%$ v/v, Patel et al.[14] found 33% v/v (deduced from

their Figure 9) and we find 20% v/v in this paper. In the work of Dayan et al., the method of preparation was very similar to ours and c^{**} was determined by optical microscopy. In the work of Patel et al., c^{**} was also measured by optical microscopy but the solution preparation process was very different from ours, their samples maturing for 20 days before use. The magnitude of 20% v/v reported herein is confirmed by calorimetric[39] and refractive index[40] measurements.

Thus for CTA it is not possible to conclude that experimental data fit Flory's theory. Another disagreement with Flory's theory is that, except for the result of Patel et al.[14], no biphasic concentration range has been found. The biphasic region as described by Patel et al.[14] is also very different to those shown by polymers which possess clearly defined biphasic regions, usually associated with a spherulitic texture of the anisotropic phase.

The results we have described indicate a relationship between the specific rotation and the conformation or rigidity of the chain. We have proposed that an increase of rigidity is associated with an increase of specific rotation. Thus the positive value of $d[\alpha]/dc$ for CTA/TFA (shown in *Figure 4*) up to the critical concentration c^{**} suggests that the chain is becoming increasingly rigid. Above c^{**}, the very large negative specific rotation due to the cholesteric liquid crystal structure[41] masks the specific rotation of the macromolecule itself. The Pincus–de Gennes theory[13] is qualitatively in accord with these results. In this theory, the chain ordering is supposed to require (a) the existence of a macromolecular coil–helix transition at a concentration c^{**} and (b) a specific intermolecular interaction between the helical macromolecules. Together, these give rise to a first-order transition at c^{**}, with no biphasic concentration range. Tsutsui et al.[10] did not observe a two-phase concentration range for cellulose derivatives, and they proposed the Pincus–de Gennes theory to be applicable to these systems. Our results for CTA support this proposal, because of the absence of the biphasic concentration range. The evidence discussed above for the macromolecular chain becoming more rigid as c approaches c^{**} also supports this proposal, as does recent calorimetric work[39].

CONCLUSION

Our experimental observations are not inconsistent with the Pincus–de Gennes theory, which requires that a coil–helix transition should take place at the isotropic–anisotropic phase change. Although we have no direct experimental proof of a molecular conformation change of this kind, our optical investigations are compatible with the proposed model for the isotropic and liquid crystalline phases.

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