

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

### Ternary Phase Equilibria for a Nitrocellulose/Solvent/Non-Solvent System

C. Viney<sup>a</sup>; A. H. Windle<sup>a</sup>

<sup>a</sup> Department of Metallurgy and Materials Science, University of Cambridge, England

**To cite this Article** Viney, C. and Windle, A. H.(1986) 'Ternary Phase Equilibria for a Nitrocellulose/Solvent/Non-Solvent System', *Liquid Crystals*, 1: 4, 379 – 396

**To link to this Article:** DOI: 10.1080/02678298608086670

**URL:** <http://dx.doi.org/10.1080/02678298608086670>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Ternary phase equilibria for a nitrocellulose/solvent/non-solvent system

by C. VINEY and A. H. WINDLE

Department of Metallurgy and Materials Science, University of Cambridge,  
Pembroke Street, Cambridge CB2 3QZ, England

(Received 25 February 1986; accepted 1 May 1986)

Phase diagrams for the system nitrocellulose/tetrahydrofuran/ethanol have been mapped out at room temperature, for two different degrees of substitution of the polymer (2.32 and 2.72). The phases formed by particular compositions were identified by using polarized light microscopy. There is a range of compositions which separate into an isotropic phase and a liquid-crystalline phase; the concentrations involved are qualitatively in agreement with Flory's theory of phase separation in a solution of rigid rod-like molecules. Our plotted room temperature sections of the phase diagrams obey the Gibbs phase rule at all points. We report evidence for the formation of a crystallosolvate of nitrocellulose (degree of substitution 2.72) and ethanol. The crystallosolvate formation only appears to be kinetically possible if there is initially also sufficient tetrahydrofuran present to dissolve the polymer.

### 1. Introduction

Molecules of nitrocellulose (NC) are chiral and semi-flexible, and they have a high aspect ratio. These characteristics are shared by the large number of different cellulose derivatives which can form a liquid-crystalline phase [1]. NC forms lyotropic phases in a variety of solvents, but does not form any thermotropic phases; the first thermally-induced transition detectable by differential scanning calorimetry (D.S.C.), on heating from room temperature, corresponds to explosive decomposition (figure 1).

Unsubstituted cellulose itself has the molecular characteristics mentioned above, but it does not readily form liquid-crystalline phases. This difference in behaviour relative to that of its derivatives reflects the difficulty in finding a system which dissolves cellulose in sufficient quantity [2, 3], and must at least in part be due to the difference in chemical regularity of the molecules. Native cellulose consists of a sequence of identical monomer units, so that, if the molecules have the local alignment synonymous with liquid-crystalline ordering, they can also easily attain the long-range lateral register necessary for them to crystallize in 3D. (For practical purposes, 'long-range' will be used to denote distances which can be resolved by optical microscopy.) Incompletely substituted derivatives, however, can be regarded as copolymers consisting of a random sequence of monomer units. Individual monomer units may be unsubstituted, monosubstituted (three possible ways), disubstituted (also three possible ways) or trisubstituted. The relative numbers of each type of unit depends on the degree of substitution (D.S.) [4]. Random copolymerization of two or three monomer types is a well-tried method of designing polymers with *thermotropic* properties over a wide and easily accessible temperature range [5]; it is reasonable to suppose that similar principles must be important in governing the formation of lyotropic phases.

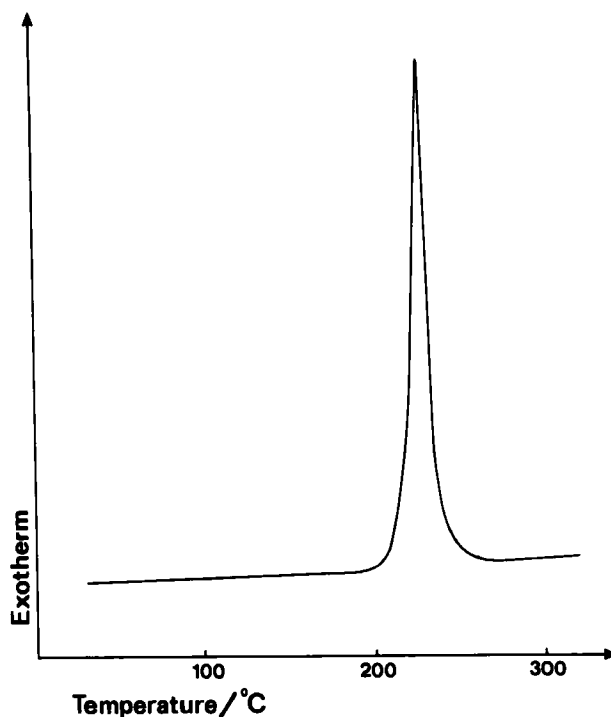


Figure 1. D.S.C. trace for NC (degree of substitution 2.72) heated from room temperature to above the detonation temperature. The specimen was heated at  $20^{\circ}\text{C min}^{-1}$ , in an inert atmosphere of dry argon provided at a flowrate of  $60\text{ ml min}^{-1}$ .

## 2. Phase equilibria in liquids containing rigid rod-like molecules

The phase behaviour of a system of rigid rods in a liquid solvent is described by the well-known theoretical work of Flory [6]. The corresponding phase diagram is plotted in figure 2(a). It shows how the actual phases observed are expected to depend on the polymer solution concentration and the interaction parameter  $X$ . This parameter is dimensionless, and represents the difference between the energy of a solvent molecule immersed in pure polymer and that of one in the pure solvent, divided by  $kT$  [7].  $X$  can therefore be changed by varying the temperature, as marked in figure 2(a). Alternatively, it may be changed by adding non-solvent to the polymer/solvent system, when it becomes more appropriate to work with a ternary phase diagram as used below. In figure 2(a), the segment of boundary drawn as a broken line indicates a range of concentrations where it has often proved difficult to obtain unambiguous experimental data. Unfavourable kinetics, leading to prohibitively long times for a particular composition to reach phase equilibrium, can be responsible for this.

Figure 2(a) has two important limitations in the context of NC/tetrahydrofuran solutions. Firstly, the Flory model is only strictly applicable to systems in which the polymer molecules are perfectly rigid rods. In the case of NC there is some flexibility due to at least partial rotational freedom about the  $\beta$ -linkages in the molecules. Secondly, the phase diagram is drawn under the assumption that the pure polymer exists in the equilibrium liquid-crystalline state over the entire temperature range to which the diagram applies. Given the X-ray evidence [8, 9] that NC has a crystalline unit cell, it is inappropriate to apply the Flory diagram as it stands [10, 11]. The

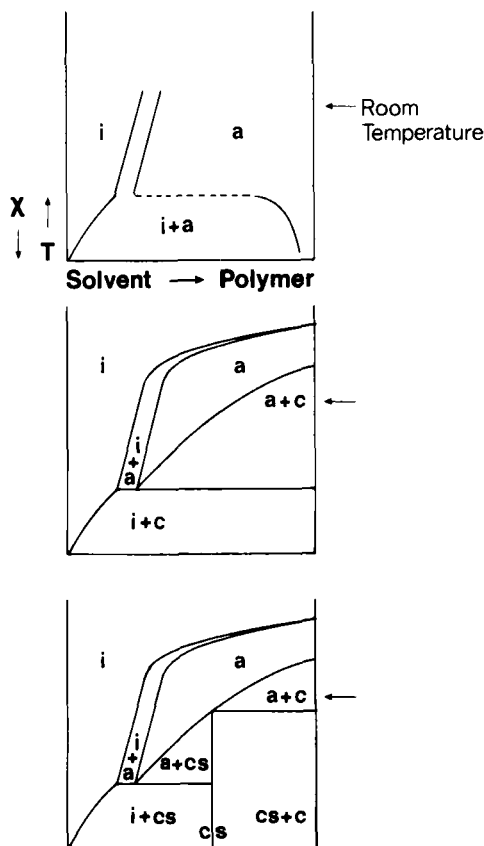


Figure 2. (a) Schematic binary diagram showing the phase separation predicted by the Flory model for a system consisting of rigid rod-like polymer molecules and a liquid solvent. (b) Schematic binary diagram similar to that shown in (a), modified in as simple a way as possible to allow for pure NC having both crystalline-liquid crystalline and liquid crystalline-isotropic transitions above room temperature. (c) Further simple modification of the binary diagram to allow for possible crystallosolvate formation.  $i$  = isotropic,  $a$  = anisotropic,  $c$  = crystalline,  $cs$  = crystallosolvate.

simplest modifications necessary to incorporate a room temperature crystalline form for NC, and to allow for crystalline-liquid crystalline and also liquid crystalline-isotropic transitions at higher temperatures, are shown schematically in figure 2(b). In practice, these transitions are not detected on heating, because detonation occurs first. The modified schematic diagram has been drawn so that it obeys the Gibbs phase rule at all points.

Figure 2(c) is a further modification of the phase diagram, to allow for the possible formation of a crystallosolvate [12]. Such a phase may be favoured when solvent can interact strongly with active groups in the polymer chains, such as the nitrate groups in NC.

Previous studies of NC lyotropic behaviour have been concerned with demonstrating the existence of an anisotropic phase, and with locating some points on the boundaries between the narrow biphasic chimney and the adjacent single-phase regions on the appropriate binary phase diagrams [1, 13]. However, no attention seems to have been given to characterizing the polymer D.S. or the molecular weight

in these investigations. The solubility of NC in a particular solvent is often strongly dependent on the D.S. We have found that tetrahydrofuran (THF) acts as a solvent over a wide range of D.S. It also dissolves the polymer relatively quickly, even compared with acetone, which, from its prominence in the literature, would appear to be the model NC solvent. In the work we report below, we used THF as the solvent, and ethanol (EtOH) as a non-solvent.

### 3. The form of ternary diagrams for polymer/solvent/non-solvent systems

When the interaction parameter  $X$  is altered by adding non-solvent to a rigid-rod polymer/solvent system, the room temperature section of the ternary phase diagram has the form shown schematically in figure 3 [12]. The phase boundaries drawn are equivalent to those shown in the binary diagram of figure 2 (a); the polymer/solvent edge of figure 3 is seen to be equivalent to an isothermal cut across the polymer/solvent binary diagram, with the effect of adding solvent being equivalent to lowering temperature. The narrow biphasic region can be discerned as in figure 2 (a).

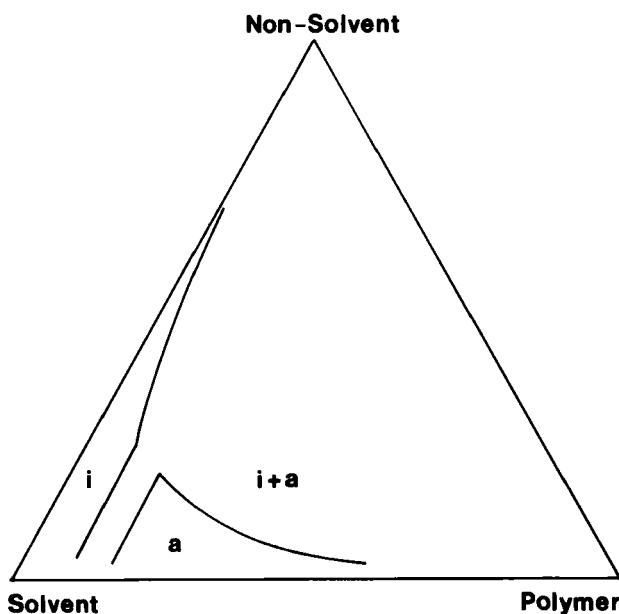


Figure 3. Schematic ternary diagram showing the phase separation predicted by the Flory model for a system consisting of rigid rod-like polymer molecules, a liquid solvent, and a liquid non-solvent.  $i$  = isotropic,  $a$  = anisotropic.

As with the simple binary diagram, however, there is the assumption that the pure polymer exists in an equilibrium liquid-crystalline form at room temperature. A more realistic schematic diagram for the polymer/solvent/non-solvent system is shown in figure 4. It has been kept as simple as possible, while obeying the Gibbs phase rule at all points and also taking account of the following observations relevant to the system NC/THF/EtOH:

- (a) Pure NC is crystallizable at room temperature.
- (b) THF and EtOH are completely miscible.

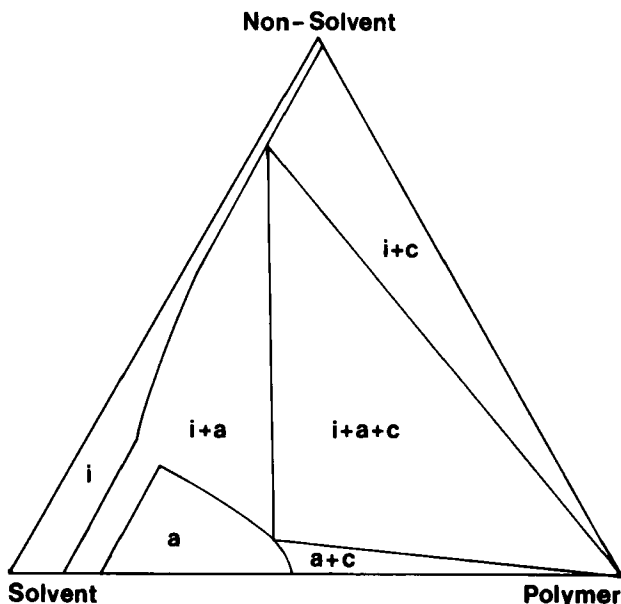


Figure 4. Ternary diagram similar to that shown in figure 3, modified in as simple a way as possible to allow for the following observations in the system NC/THF/EtOH: (a) pure NC is crystalline at room temperature; (b) THF and EtOH are completely miscible; (c) EtOH dissolves hardly any polymer. *i* = isotropic, *a* = anisotropic, *c* = crystalline.

- (c) EtOH dissolves practically no polymer at *room temperature*. (Dissolution of NC in EtOH does occur slowly at temperatures below  $\sim -75^{\circ}\text{C}$  [14].)

The diagram has to be presented schematically because the positions of the boundaries will depend on polymer D.S. and molecular weight. Also, the 'crystalline' phase in equilibrium with isotropic or anisotropic NC solutions may have a different structure from as-nitrated cellulose.

#### 4. Experimental determination of the room temperature section through the NC/THF/EtOH ternary diagram

##### 4.1. The as-received NC

Two polymers were used, having the following two different degrees of substitution:

- (a) D.S. = 2.32. Source: manufactured from wood pulp by the displacement process, at the Royal Ordnance Factory, Bishopton.
- (b) D.S. = 2.72. Source: manufactured from cotton linters by the mechanical nitration process, at the Royal Ordnance Factory, Bishopton.

##### 4.2. Preparation of samples of known composition

A qualitative test for the presence of a liquid-crystalline phase involves the observation of solution turbidity. The turbidity arises when domains of ordered molecules form in sufficient number on an optically detectable scale, and with sufficiently sharp discontinuities in optical orientation between them, for significant light

scattering to occur. Since impurities suspended in sufficient concentration in the solutions can also scatter light, it is important to reduce their concentration first. The following method was used to purify as-received polymer: the NC was dried in an oven at 60°C and allowed to cool to room temperature in a desiccator. It was dissolved in excess THF, and the solution was filtered through a cotton wool plug. The NC was re-precipitated by adding an excess of distilled water, collected, and dried. NC processed in this way is still found to contain some insoluble impurities (see, for example, figure 7), but to a lesser extent than the as-received material. A higher degree of purity might be obtained by using filter paper instead of a cotton wool plug during filtration, but the viscosity of even dilute solutions is high enough to make the passage of such solutions through filter paper prohibitively slow.

The D.S. of the purified polymer is thought to be little changed from that of as-received NC, since very little material is actually rejected during processing.

NC/THF solutions of a given concentration can of course be made up by weighing out a known amount of polymer and adding an appropriate amount of solvent. However, the kinetics of this route are slow, especially for concentrated solutions, and it is uncertain whether equilibrium is attained in these systems [11]. In other words it is difficult to decide whether, in a sample containing discernible solid and liquid phases, the system is genuinely two-phase, or whether further dissolution of the solid is unfavourable kinetically. To help overcome this difficulty, our experiments were conducted on solutions prepared via a different route: a known mass of polymer was dissolved completely in sufficient THF to give a 2 vol% solution; the solvent was then allowed to evaporate at room temperature until the solution had a mass equal to that calculated to correspond to the desired concentration.

For ternary compositions requiring the presence of non-solvent, EtOH was added to a system already containing NC and THF in the required ratio. Individual points on the phase diagram were therefore accessed by following the procedure summarized in figure 5.

#### 4.3. Recognition of phases present

By viewing the systems macroscopically, it is possible to make some (mainly qualitative) deductions as to the phases present. A clear liquid or gel is isotropic, while

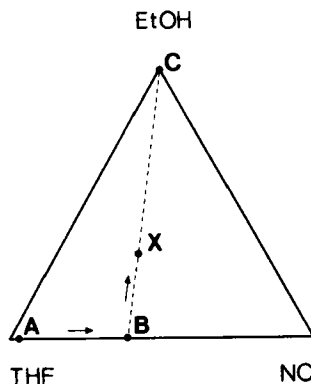


Figure 5. Graphical representation of the method used to produce a specimen having a given composition X: (a) dissolve NC in THF to give a 2 vol% solution (point A); (b) evaporate solvent until solution has the same NC:THF ratio (point B) as the given composition X. Note that all points lying on BXC have the same NC:THF ratio; (c) add sufficient EtOH to obtain composition X.

a turbid liquid or gel may suggest either a single optically anisotropic phase or a multi-phase system. A liquid floating above gel-like or solid material also indicates a multi-phase region on the phase diagram; in this last case, it may be possible to use the lever rule to *estimate* how far the stated composition plots from the boundaries of the region.

Unambiguous assessment of the phases present requires samples to be withdrawn for optical microscopy. To reduce solvent/non-solvent loss during microscopic observation, samples were held in a simple cell constructed from a glass microscope slide, cover slip, polyethylene spacer (thickness  $\sim 10\ \mu\text{m}$ ) and bulldog clips (figure 6). The cell has been shown to be an effective container of the volatile solvent/non-solvent: in several control experiments, the weight loss of volatiles, relative to the amount originally present, was never found to be more than 2.5 per cent over a period of 7 days, even for specimens consisting entirely of THF/EtOH.

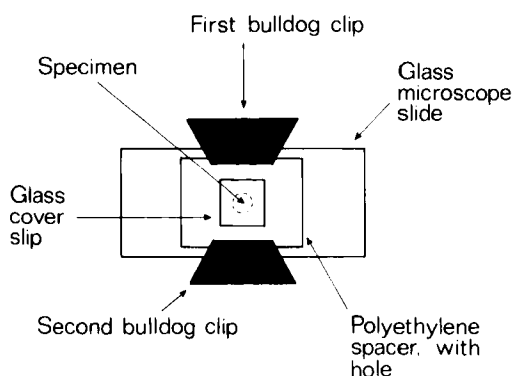


Figure 6. Schematic representation of cell used to contain samples for optical microscopy.

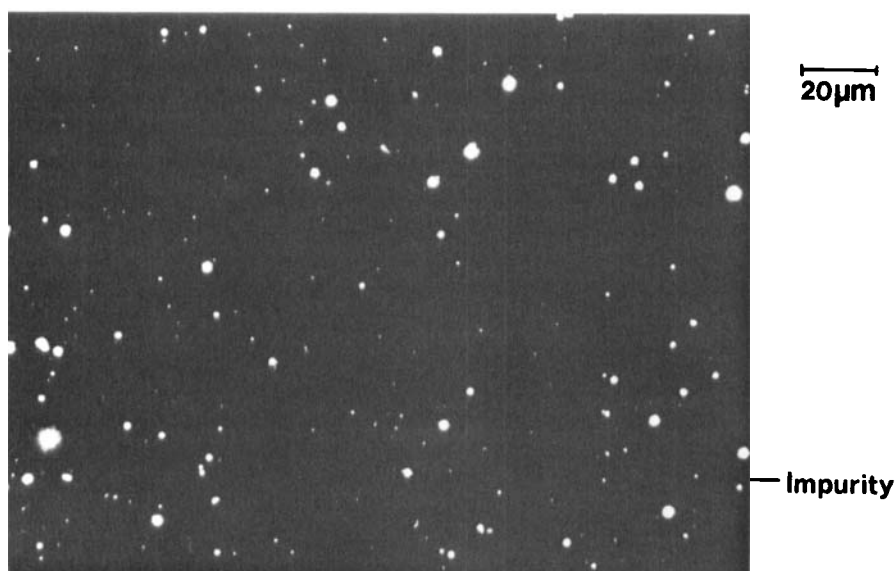


Figure 7. Micrograph typical of compositions plotting in the isotropic phase field of a NC/THF/EtOH phase diagram. Crossed polars; polarizer transmission direction horizontal.



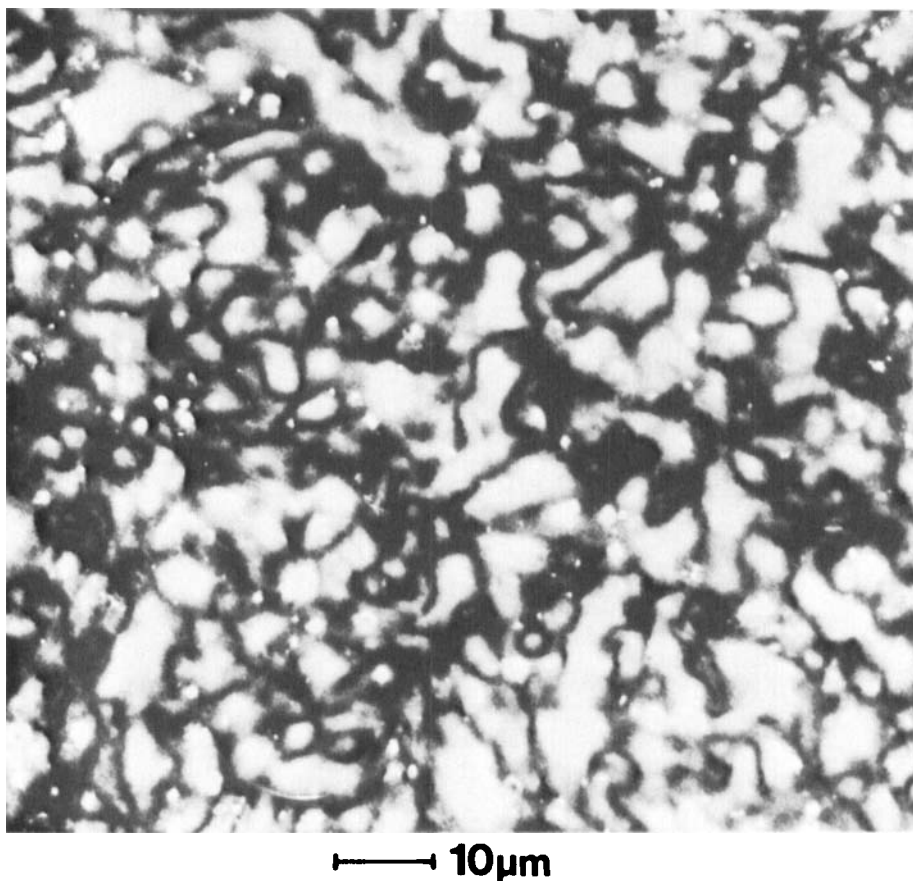


Figure 8. Optical texture typical of compositions plotting in the anisotropic single-phase field of a NC/THF/EtOH phase diagram. Crossed polars; polarizer transmission direction horizontal.

The scale of the microstructures changes with time; the micrographs discussed below were obtained within a few hours of the thin samples being prepared. It must be stressed that, in this type of study, one relies on either the individual domains or aggregates of domains being sufficiently large for the optical microscope to resolve them.

Different regions on the phase diagram can be identified microscopically as follows:

- (a) Isotropic (liquid). The specimen consists of a clear fluid which does not transmit light when viewed between crossed polars. There are however a number of approximately micron-sized, birefringent, insoluble impurities (figure 7), which are also clearly visible when the specimen is viewed microscopically in unpolarized light.
- (b) Anisotropic (liquid or gel-like, depending on concentration). The optical microstructure has the characteristics of a liquid-crystalline texture (figure 8), i.e. the specimen is birefringent though not of uniform optical orientation. Individual regions extinguish four times per  $360^\circ$  rotation of the crossed polars. The textures observed usually resemble those typical of nematic liquid crystals, often containing the extinction band patterns characteristic of dis-

clinations of strength  $\pm \frac{1}{2}$  and strength  $\pm 1$ . Occasionally, the textures contain oily streaks or Grandjean walls, and are then more suggestive of a cholesteric liquid crystal. The ambiguity is resolved by noting that cellulose derivatives are chiral and therefore bound to be cholesteric [15], but the pitch of the associated helix is large, so that even over distances of several microns the molecular ordering approximates to being nematic [16]. This could also explain why we have not observed 'fingerprint' textures—the pitch is too large compared with typical domain sizes in the microstructures. The viscosity of the solutions may be high enough to delay the development of full cholesteric ordering, relative to the time taken to form nematic textures.

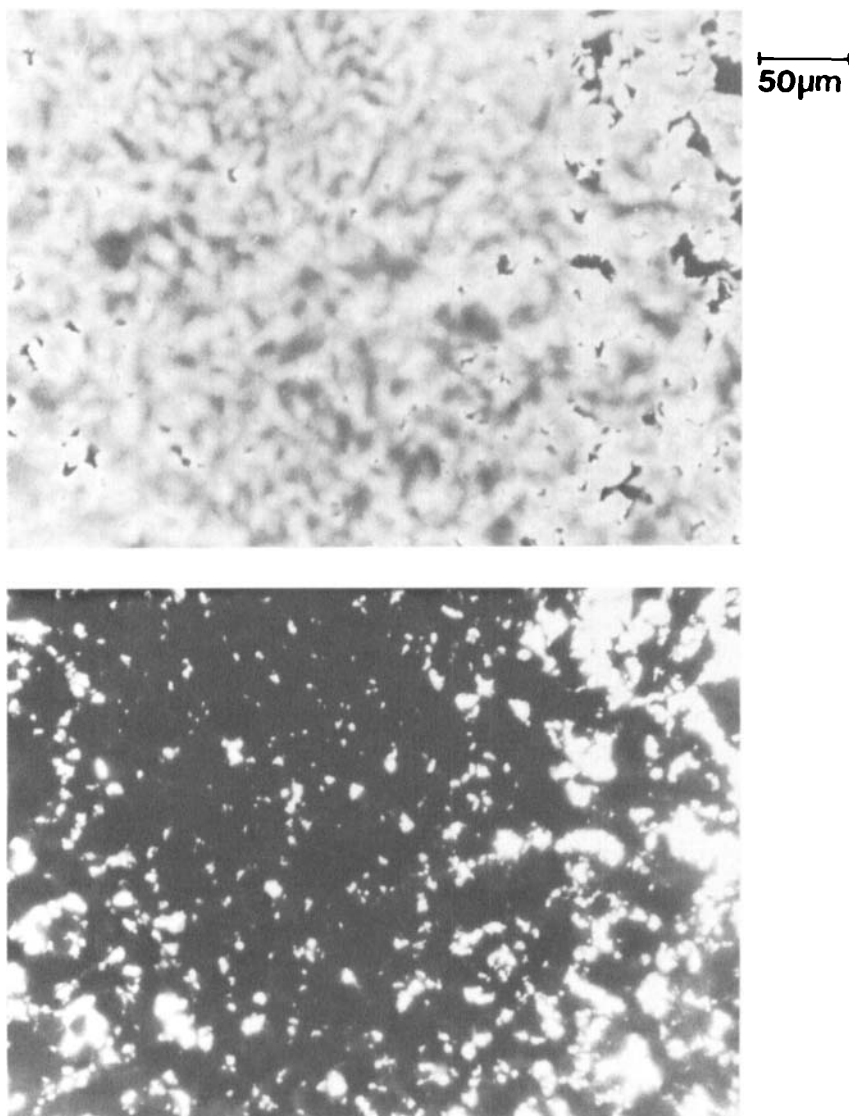


Figure 9. Grains of purified NC, photographed between crossed polars (top; polarizer transmission direction horizontal) and in unpolarized light (bottom). The black areas observed between crossed polars occur where there is no polymer.

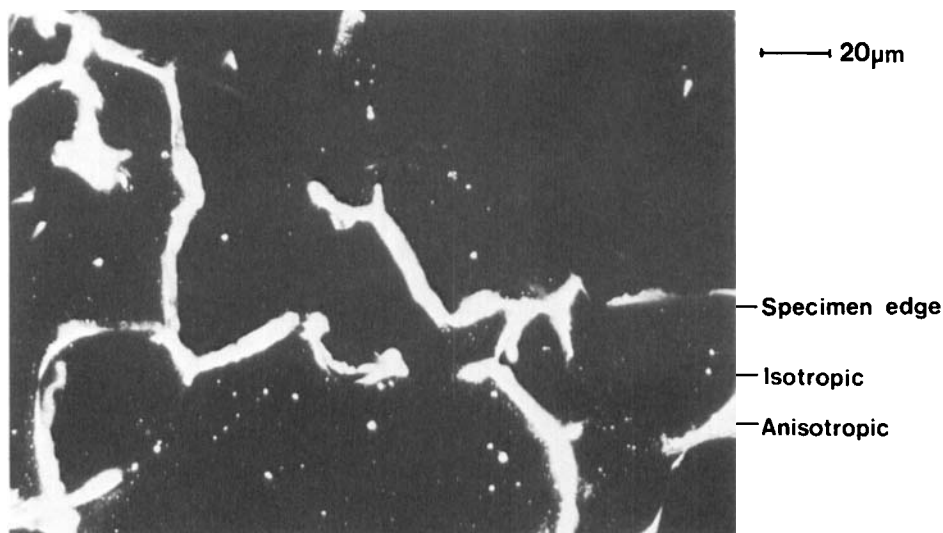


Figure 10. Micrograph typical of compositions plotting in the isotropic+anisotropic two-phase field of a NC/THF/EtOH phase diagram. The presence of insoluble impurities in the isotropic regions allows them to be distinguished from areas of the slide where there is no specimen. Crossed polars; polarizer transmission direction horizontal.

- (c) Crystalline (solid). The individual grains of purified NC can be distinguished microscopically between crossed polars or in unpolarized light (figure 9). The grains themselves consist of many barely resolvable crystalline entities.
- (d) Isotropic + anisotropic (liquid). Macroscopically, there is no visible phase separation. The optical microstructure between crossed polars (figure 10) consists of a mixture of regions which show extinction for all rotations of the crossed polars (isotropic) and regions which are birefringent (anisotropic). The latter regions are readily broken up by displacing the cover slip. In a given specimen, the boundaries between regions may change in position and shape with the passage of time (growth and coarsening). The area of the phase diagram which is associated with such two-phase behaviour is often referred to as *the* 'biphasic' or *the* 'heterogeneous' region [6, 12, 13], since it is usually the *only* two-phase region to be studied. The lever rule may be used to estimate how far a particular composition lies from the boundaries with the isotropic and anisotropic single-phase regions. However, it must be stressed that the lever rule can only give an *estimate*, since, in the absence of further information such as the chemical compositions of the two coexisting phases, the exact direction of tie-lines is unknown [17]. The higher the birefringence of the anisotropic phase, the greater the polymer content can be presumed to be, giving some guidance as to the probable direction of the tie-line.
- (e) Anisotropic + crystalline (gel-like). Macroscopically, there is no visible phase separation. Coexistent with the textures of the liquid-crystalline phase, are regions having the optical characteristics of the purified NC: they are clearly visible in unpolarized light as well as between crossed polars (figure 11). In the latter case, their contrast and visibility is independent of the crossed polar rotation relative to the specimen, confirming that they consist of a large number of superimposed submicroscopic domains.

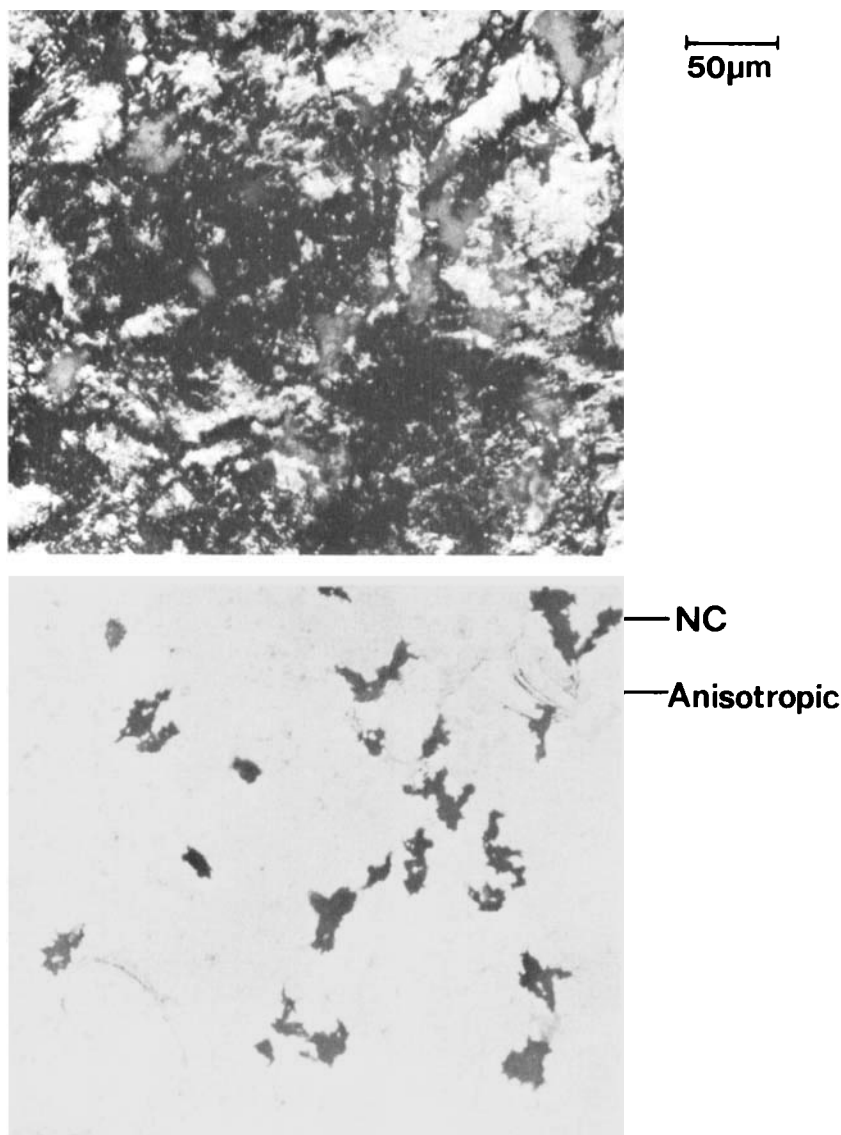


Figure 11. Micrographs typical of compositions plotting in the anisotropic + crystalline two-phase field of a NC/THF/EtOH phase diagram. Top: crossed polars; polarizer transmission direction horizontal. Bottom: no polars.

- (f) Isotropic + crystalline. Macroscopically, the system separates into a precipitate and a clear supernatant liquid. The precipitate has the same microscopic optical characteristics as the purified NC, and the liquid is microscopically indistinguishable from the isotropic phase described earlier.
- (g) Isotropic + anisotropic + crystalline. Macroscopically, the system separates into a precipitate and a clear supernatant liquid. The precipitate has a microstructure similar to that of compositions which plot in the 'anisotropic + crystalline' field of the phase diagram, while the liquid is again microscopically indistinguishable from the isotropic phase described previously. As with

the two-phase regions, it is not possible to use the lever rule to define the position of the boundaries of the three-phase region relative to a particular composition. However, once the corners of the three-phase region have been fixed, it is possible to draw in the boundaries, since these are necessarily straight lines [17]. It is also possible to check whether the corners have been correctly placed, since they define the compositions of the phases in equilibrium for *any* overall composition that plots within the three-phase region, and the relative amounts of each phase can be calculated from the presumed phase diagram and compared with actual measurements.

In general, the position of phase boundaries on the experimentally determined phase diagram was found by observing which phases are detectable in each of a large number of different compositions, while using the lever rule as a guide to obtaining compositions increasingly close to any particular phase boundary.

### 5. Results and discussion

Figures 12 and 13 show the room temperature sections through the ternary phase diagrams for NC/THF/EtOH, for polymer having a D.S. equal to 2.32 and 2.72 respectively. There is qualitative agreement with the schematic diagram predicted in figure 4.

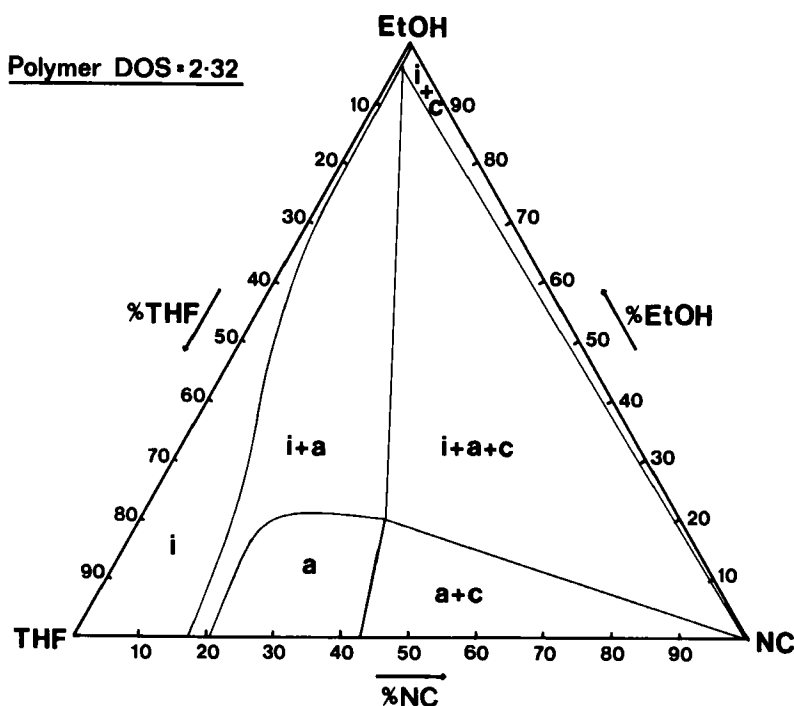


Figure 12. Experimentally determined room temperature section through the ternary phase diagram for NC/THF/EtOH, for a polymer D.S. of 2.32.

The concentrations of NC in THF required both for initial appearance and for complete formation of a liquid-crystalline phase are lower for the more highly nitrated polymer. Usually, such a trend can be ascribed to a difference in molecular weight, a higher molecular weight implying a higher molecular aspect ratio and a smaller

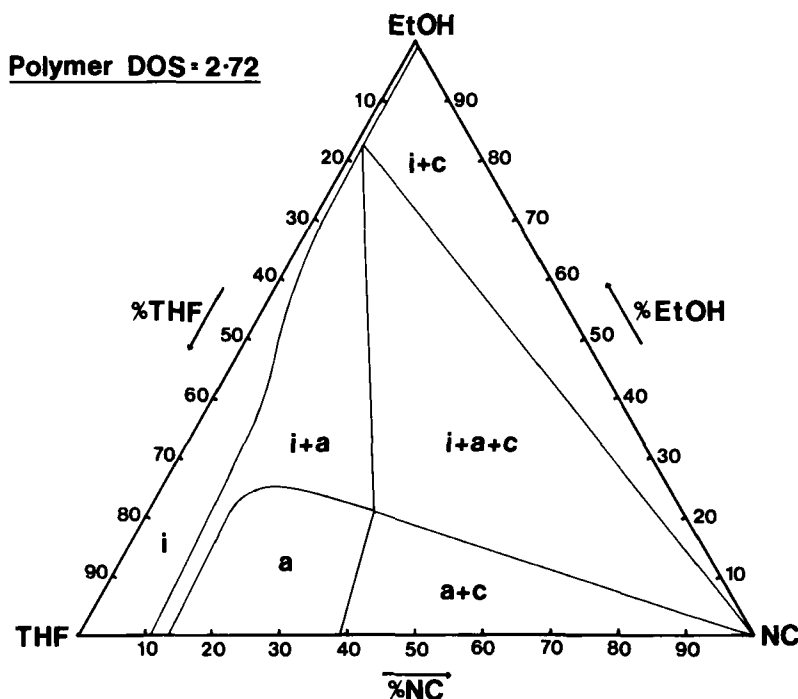


Figure 13. Experimentally determined room temperature section through the ternary phase diagram for NC/THF/EtOH, for a polymer D.S. of 2.72.

critical concentration required for the formation of a liquid-crystalline phase [6]. However, although the molecular weight of NC apparently does not depend strongly on D.S. [8], the tendency is for more highly nitrated polymer to have a *lower* molecular weight. The apparently enhanced liquid crystal forming ability must therefore depend on other factors. For example, the greater probability of finding similar domains of monomers on adjacent molecules may promote the formation of domains on an optically resolvable scale.

The more polymer-rich compositions plotting within the chimney of the isotropic + anisotropic two-phase field were found to exhibit macroscopic turbidity. (Such compositions typically contained at least 2 vol% more polymer than those having the same THF : EtOH ratio but plotting on the isotropic/isotropic + anisotropic boundary.) Thus, if a series of compositions confined to sealed tubes is heated or cooled, it is possible to estimate how the position of this boundary changes with temperature, by observing whether the specimens are turbid or not.

Specimens were heated by immersion in a water bath at 40°C, or cooled by placing in a deep-freeze at -27°C. Heating to 40°C moves the isotropic/isotropic + anisotropic boundary to the right, to compositions containing about 5 vol% more polymer at a given THF : EtOH ratio, relative to its position at room temperature (~20°C). Cooling to -27°C has a similar order of magnitude effect, but the boundary is shifted towards the left. These results are observed for a polymer D.S. of 2.32 and also for one of 2.72.

The observed positive direction of slope of the isotropic/isotropic + anisotropic boundary agrees with that predicted theoretically (figure 2(a)) for solvent/polymer (two-component) sections through the ternary phase diagrams.

The polymer molecular weight, for both degrees of substitution, is of the order of  $M_N \sim 7 \times 10^4$ . From this figure, assuming the molecules to be rigid rods, a molecular aspect ratio of  $\sim 200$  can be estimated. In figures 12 and 13, the chimney intersects the THF-NC axis at polymer concentrations somewhat higher than that predicted by Flory's theory [6] ( $\sim 0.05$  for molecules with an aspect ratio of  $\sim 200$ ). This quantitative difference can be seen as evidence for some degree of molecular flexibility.

### 6. Formation of a crystallosolvate phase

The isotropic supernatant phase formed by compositions plotting in the three-phase field of the diagram for the D.S. = 2.72 polymer has an unexpected property. If it is removed from the remainder of the system and allowed to evaporate from a glass microscope slide, a solid residue having the textures shown in figure 14 (a) to (c) is observed between crossed polars. The first material to be deposited does not form a continuous phase (for example, figures 14 (a), (b), but the last fraction does (figure 14 (c)). The implication is that, between the composition of the isotropic liquid (always constant if it is formed in a three-phase system) and that of the deposited material, there is a range of compositions in which the isotropic liquid and the deposited material are in equilibrium. These compositions can only be accessed kinetically by evaporating the volatile components from the isotropic liquid.

Over a period of a week, the deposited solid loses contrast in the polarizing microscope, and eventually has the appearance of the crystalline (purified NC) phase described earlier. A similar change in microstructure is observed if the deposited material is heated rapidly to above  $150^\circ\text{C}$  in a microscope hot stage. On subsequent cooling there is no further change in microstructure. If alternatively the material is heated to temperatures lower than  $150^\circ\text{C}$ , the textures of figure 14 are lost over a period of time inversely related to the temperature. These observations point to there being some residual solvent/non-solvent bound in the deposited material at room temperature.

A D.S.C. trace of the deposited material is shown in figure 15 (a). The two endotherms (at  $\sim 153^\circ\text{C}$  and  $\sim 172^\circ\text{C}$  for a heating rate of  $20^\circ\text{C min}^{-1}$ ) are shifted to higher temperatures if the heating rate is increased. The exotherm at  $220^\circ\text{C}$  represents explosive decomposition of NC. If, alternatively, the deposited material is heated to  $160^\circ\text{C}$  (figure 15 (b)), held at that temperature for 2 min, cooled to room temperature, and reheated, it is found that *both* endotherms are missing during the re-heat (figure 15 (c)). These results too are consistent with there being solvent/non-solvent bound in the deposited material at room temperature. The first endotherm on heating (figure 15 (a)) may be identified with the solvent/non-solvent debonding from the polymer, and the second endotherm then represents evaporation of the solvent/non-solvent.

It is possible to use infrared (I.R.) spectroscopy to identify the components present in the deposited material. NC can be identified unambiguously by its strong absorption at wavenumbers around  $1640\text{ cm}^{-1}$  (double-bond stretching in  $\text{ONO}_2$  [18]). EtOH is characterized by a very strong peak at  $\sim 3200\text{ cm}^{-1}$  (O-H bond stretching [18]; the peak is far more pronounced than that obtained from unsubstituted O-H when NC is scanned). The most significant unique absorption in the THF (due to symmetric ring stretching [19]) occurs at  $900\text{ cm}^{-1}$ . A *rough* guide to the relative amounts of these components present in a particular system is given by comparing the relative intensities of the different peaks. The original liquid formed by compositions plotting in the three-phase field on the phase diagram is found to contain rather more EtOH

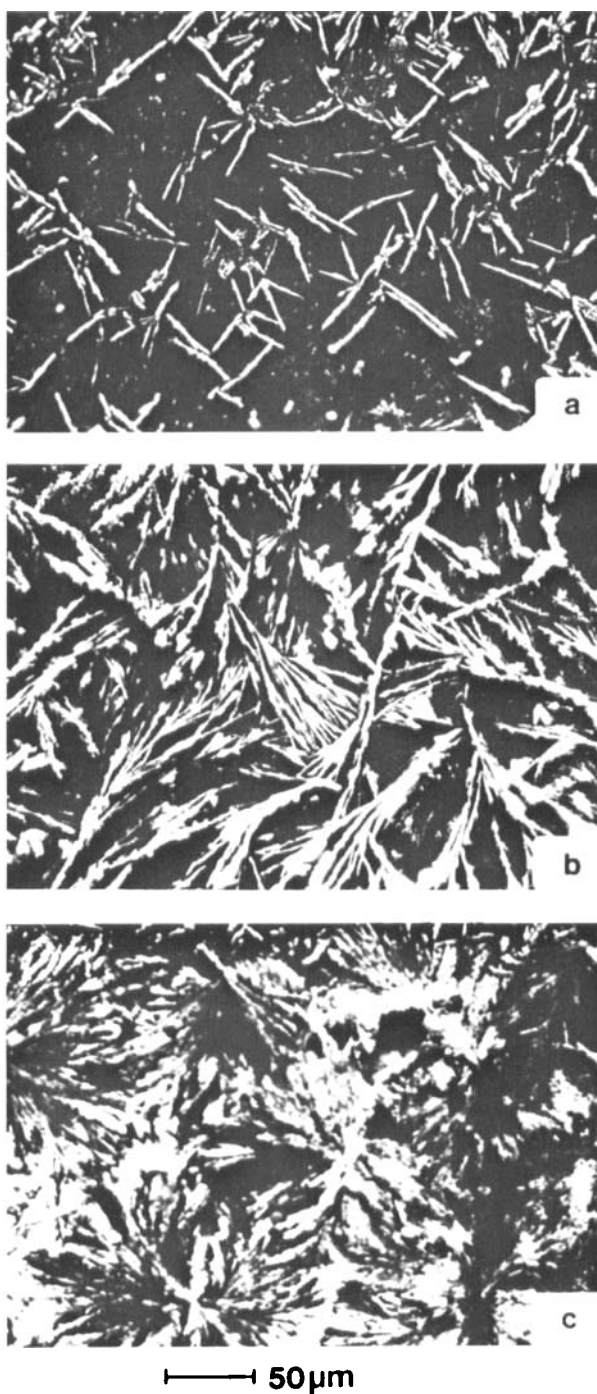


Figure 14. Microstructure of the deposit which forms on evaporating the isotropic phase that separates from compositions plotting in the three-phase field of figure 13. (a) Shows the morphology of the first material that is deposited. (b) Shows material nucleated and grown subsequently to (a). (c) Shows the last fraction of material to be deposited. Crossed polars; polarizer transmission direction horizontal.



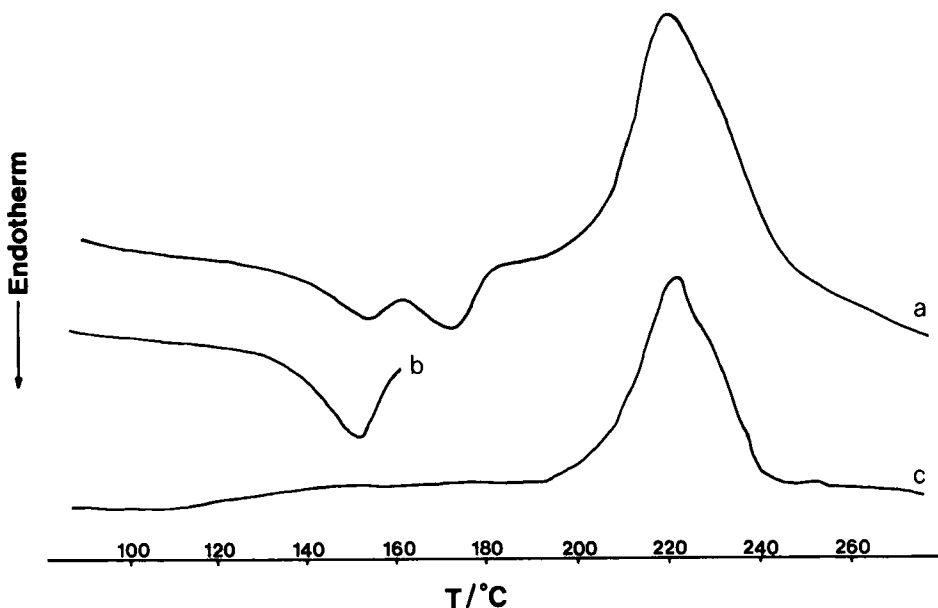


Figure 15. D.S.C. traces of material shown in figure 14. Specimens were heated at  $20^{\circ}\text{C min}^{-1}$ , in an inert atmosphere of dry argon provided at a flowrate of  $60\text{ ml min}^{-1}$ . (a) Trace of as-deposited material being heated to above the explosive decomposition temperature. Two endotherms (at  $\sim 153^{\circ}\text{C}$  and  $\sim 172^{\circ}\text{C}$ ) and an exotherm (at  $\sim 220^{\circ}\text{C}$ ) are observed. (b) Trace of as-deposited material being heated to  $160^{\circ}\text{C}$ . (c) Trace of the material used in (b), after holding at  $160^{\circ}\text{C}$  for 2 min and cooling to room temperature, being heated to above the explosive decomposition temperature. Both of the endotherms detected in (a) have disappeared.

and less THF and NC, in qualitative agreement with its position on the phase diagram. The residue left after evaporation of the volatile fraction contains NC and EtOH, but *no* detectable amount of THF.

One is led to regard the deposited material as a crystallosolvate formed from NC and EtOH. It is not clear why such a phase is not formed with the polymer having the lower D.S. (2.32). It is however known that, within the overall D.S. range 2.32 to 2.72, the D.S. for *primary* substitution increases from a fractional value to unity; it may be necessary for the primary site to be regularly (and therefore fully) substituted to enable formation of the crystallosolvate structure. It has not proved possible to produce the crystallosolvate by adding EtOH directly to NC. The only route found is the one described above, suggesting that there are important kinetic factors in the formation of this phase.

By measuring the weight lost when the crystallosolvate is heated to above  $160^{\circ}\text{C}$  and held at that temperature for a few minutes, the volume fraction of EtOH is estimated as being  $\sim 0.75$ .

The commercially available THF used in this study contains  $\sim 0.1$  per cent hydroquinone (quinol) as a stabilizer against peroxide formation. Since the crystallosolvate appears as THF is lost by evaporation, one must consider the possibility that the non-volatile stabilizer becomes relatively more concentrated, and thus may contribute to the crystallosolvate formation. As a check, therefore, THF was distilled (after adding  $\text{LiAlH}_4$  to destroy any peroxides and to ensure a water-free distillate); it was used immediately to prepare further samples plotting in the three-phase field on the

NC (D.S. = 2.72)/THF/EtOH phase diagram. When evaporated from a glass microscope slide, the isotropic supernatant phase yielded the crystallosolvate as before.

Figure 16 shows, in schematic and exaggerated form, the simplest changes which must be made to the room temperature section of the NC (D.S. = 2.72)/THF/EtOH phase diagram in order to accommodate a crystallosolvate phase.

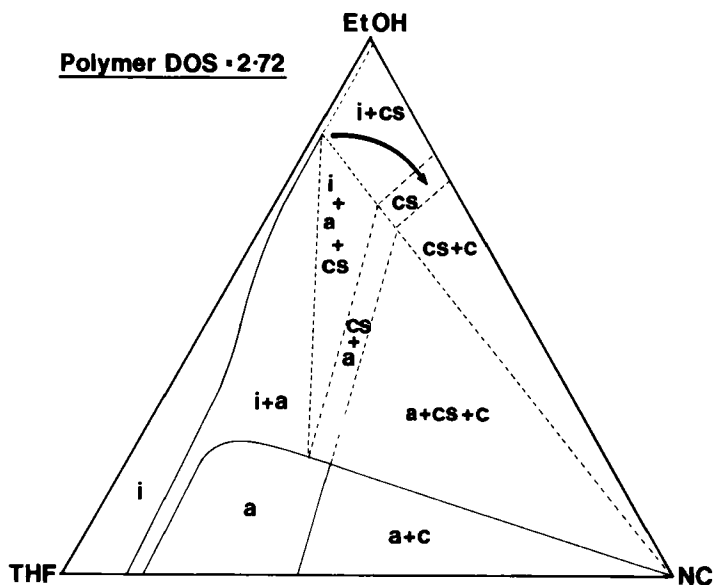


Figure 16. Schematic representation of the simplest changes which must be made to the room temperature section of the NC (D.S. = 2.72)/THF/EtOH phase diagram in order to allow for the existence of a crystallosolvate phase. Broken lines have been used where the position of a boundary is uncertain.

It is interesting to note that the crystallosolvate shows normal interference colours, whereas pure NC has anomalous colours. The birefringence is approximately  $-0.1$ , which is more than an order of magnitude higher than the birefringence ( $-0.006$  [20]) of as-nitrated polymer having the same D.S. The negative sign is written to take account of the fact that the acicular growth entities (figures 14(a), (b)) are length fast, and that the circularly symmetric growth bodies (figure 14(c)) are fast in the radial direction.

An alternative route for obtaining an interaction between NC and EtOH exists at low temperatures ( $\sim -75^{\circ}\text{C}$ ), where NC will dissolve in EtOH on a timescale measured in days [14]. It would be interesting to compare the X-ray diffraction pattern of NC which has been swollen by EtOH under these conditions, with a pattern from the crystallosolvate described earlier in this paper.

## 7. Conclusions

(1) By using polarized light microscopy, it has been possible to map out room temperature sections of the ternary phase diagrams for nitrocellulose/tetrahydrofuran/ethanol, for nitrocellulose having degrees of substitution equal to 2.32 and 2.72.

(2) With both polymers, we have found that there is a range of ternary compositions for which the system separates into an isotropic and a liquid-crystalline phase. The representation of this separation on the phase diagrams is qualitatively in

agreement with the predictions of Flory's model for a system based on a solution of rigid rods.

(3) There is evidence for formation of a crystallosolvate consisting of nitrocellulose (degree of substitution 2.72) and ethanol. Its formation appears to be unfavourable kinetically, unless there is initially sufficient solvent (tetrahydrofuran) present to dissolve the polymer. The crystallosolvate shows normal interference colours, is optically negative, and has a birefringence approximately an order of magnitude higher than that of the pure polymer.

We are grateful to RARDE for funding, to Dr. T. J. Lewis, Dr. F. S. Baker and Professor P. J. Flory for valuable discussions, and to Professor D. Hull for providing laboratory facilities.

### References

- [1] GRAY, D. G., 1983, *J. appl. Polym. Sci., Appl. Polym. Sympos.*, **37**, 179.
- [2] CHANZY, H., PEGUY, A., CHAUNIS, S., and MONZIE, P., 1980, *J. Polym. Sci., Polym. Phys. Edit.*, **18**, 1137.
- [3] BIANCHI, E., CIFERRI, A., CONIO, G., COSANI, A., and TERBOJEVICH, M., 1985, *Macromolecules*, **18**, 646.
- [4] CLARK, D. T., STEPHENSON, P. J., and HEATLEY, F., 1981, *Polymer*, **22**, 1112.
- [5] WINDLE, A. H., VINEY, C., GOLOMBOK, R., DONALD, A. M., and MITCHELL, G. R., 1985, *Faraday Discuss. chem. Soc.*, **79**, 55.
- [6] FLORY, P. J., 1956, *Proc. R. Soc. A*, **234**, 73.
- [7] FLORY, P. J., 1953, *Principles of Polymer Chemistry* (Cornell University Press), p. 509.
- [8] MILES, F. D., 1955, *Cellulose Nitrate* (Oliver & Boyd).
- [9] TROMMEL, J., 1959, *The Molecular Arrangement of Cellulose Nitrates* (Communication No. 15 from the N. V. Koninklijke Nederlandsche Springstoffenfabrieken, Amsterdam).
- [10] CIFERRI, A., and KRIGBAUM, W. R., 1981, *Molec. Crystals liq. Crystals*, **69**, 273.
- [11] PAPKOV, S. P., 1977, *Contemporary Topics in Polymer Science*, Vol. 2, edited by E. M. Pearce and J. R. Schaefgen (Plenum Press).
- [12] PAPKOV, S. P., 1984, *Adv. Polym. Sci.*, **59**, 75.
- [13] AHARONI, S. M., 1981, *Polym. Prepr.*, **22**, 116.
- [14] NEWMAN, S., KRIGBAUM, W. R., and CARPENTER, D. K., 1956, *J. Phys. Chem.*, **60**, 648.
- [15] GRAY, D. G., 1985, *Faraday Discuss. chem. Soc.*, **79**, 257.
- [16] GRAY, D. D., 1985 (personal communication).
- [17] COTTRELL, A. H., 1975, *An Introduction to Metallurgy* (Edward Arnold), Chap. 16.
- [18] WILLIAMS, D. H., and FLEMING, I., 1973, *Spectroscopic Methods in Organic Chemistry* (McGraw-Hill).
- [19] BARROW, G. M., and SEARLES, S., 1953, *J. Am. chem. Soc.*, **75**, 1175.
- [20] LEWIS, T. J., 1982, *Polymer*, **23**, 710.