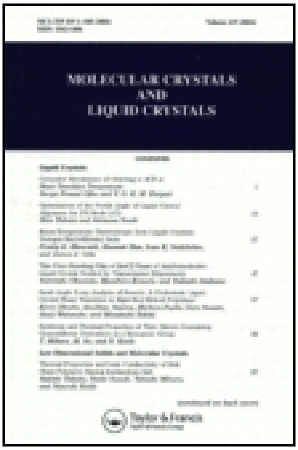

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Lyotropic Behaviour of Nitrocellulose

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Lyotropic Behaviour of Nitrocellulose

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Recent work on the ternary system nitrocellulose (NC)/tetrahydrofuran (THF)/ethanol (EtOH) has yielded the room temperature section through the phase diagram. Separation into isotropic and anisotropic phases is observed within limits qualitatively in agreement with Flory's theory for the phase separation of rigid rod/solvent/non-solvent systems. The equilibrium arrangement of molecules in the mesophase favours a layered structure, consistent with their chiral nature. Given sufficient time, a crystallosolvate of NC and EtOH is formed by some ternary solutions; this confirms our choice of EtOH as a non-solvent with a significant effect on the polymer-environment interaction parameter. Aligned reconstituted NC can be produced from single-phase anisotropic solutions or from two-phase isotropic + anisotropic solutions in THF/EtOH. In the latter case, nematic-like order may be induced in the isotropic phase by a suitably high shear. The reconstituted fibres do not contain any detectable amount of crystallosolvate. Considerable local reinforcement between chains in the solid polymer may arise from the formation of "non-periodic layer" crystallites.

Keywords: lyotropic polymers, nitrocellulose

INTRODUCTION

Main chain liquid crystal-forming polymers characteristically consist of rigid or semi-rigid units linked to form molecules with a high aspect ratio. Most importantly, if a thermotropic phase is to be formed at conveniently accessible temperatures, or if the polymer is to have sufficient solubility to form a lyotropic phase, the molecular architecture should not favour long crystallisable runs of subunits.[1,2] These considerations underlie the synthesis of a large variety of thermotropic copolyesters,[3] where full three-dimensional crystallinity is discouraged by the random sequence of monomers in the chains. Intractability is also reduced by the use of asymmetrically substituted units, and units which contain rigid kinks or flexible bonds.

Native cellulose consists of extended chains[4] of β-linked 1,4 anhydroglucose units, and is therefore a homopolymer. Two linked monomers are shown in Figure 1. There are few solvents capable of dissolving cellulose, and very few are strong enough to form solutions in which the cellulose concentration is sufficiently high for mesophase formation to occur.[5-7] On the other hand, a rapidly growing number of cellulose *derivatives* has been shown to exhibit both thermotropic and lyotropic properties.[8,9] There are several possible ways, not simply related, in which the addition of sidegroups can alter the mesophase-forming ability of the cellulose chains: they increase chain stiffness by impeding rotation about the glycoside bridges in the chain, and they can render the polymer molecules more accessible to the solvent. Also, by increasing the chain diameter, they reduce the aspect ratio (x), and increase the critical concentration (v_2^* required for the formation of lyotropic mesophases. This follows from Flory's equation[10]

$$v_2^* \sim (8/x)(1-2/x)$$

(The precise way in which x is defined in this context depends on whether one is dealing with a fully rigid polymer, a semi-flexible one, or one consisting of a series of freely jointed rods.[8]) Furthermore, either a high degree of substitution by bulky sidegroups, or nonuniform substitution by small sidegroups, can inhibit crystallisation. In the last respect, the effect of random substitution is similar to that of random copolymerisation as described above.

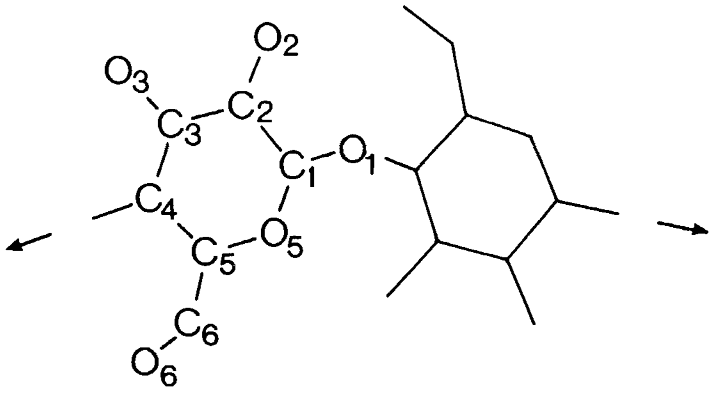

FIGURE 1 Schematic representation of two β-linked glucose residues (no hydrogen atoms shown), with the conventional numbering of carbon and oxygen atoms.

Nitrocellulose (NC) is an ester produced commercially by the reaction between cellulose and mixed nitric and sulphuric acids. The nitration process initially favours substitution at the C(6) site (Figure 1), since this is the one most accessible to the nitrating medium. At a degree of substitution (DS) of 2.62, all these so-called primary sites are nitrated, and the number of mononitrated glucose residues has decreased to zero.[11] Above this nitration level, the polymer consists of a random sequence of three monomer types: 2,6-dinitrated, 3,6-dinitrated, and 2,3,6-trinitrated.

The possibility of producing lyotropic solutions of NC is interesting because it provides a route for drawing fibres of reconstituted material having a high degree of molecular alignment.[12] Such fibre will be useful for x-ray diffraction studies of the preferred conformation of NC molecules, independent of any structure dictated by the cellulose source organism. Nitrocellulose forms anisotropic solutions in at least 24 solvents[8]; our own work has centred on NC/tetrahydrofuran (THF)/ethanol (EtOH) systems, where THF acts as a solvent and EtOH as a non-solvent.[13] The room temperature section of the NC/THF/EtOH phase diagram is reproduced in Figure 2, for polymer having a DS of 2.72 and $M_n \sim 7.10.^4$ Areas associated with the formation of a NC/EtOH crystallosolvate are demarcated by broken lines, because of uncertainty regarding the exact compositions involved.[13] The existence of the crystallosolvate confirms the choice of EtOH as a non-solvent having a significant effect on the polymer-solvent interaction parameter.

In the present work, we investigate the nature of the ordering in the anisotropic phase, and we discuss the changes in supramolecular ordering that result from shearing single phase anisotropic compositions and also biphasic isotropic/anisotropic compositions. Our observations are relevant to the choice of conditions under which reconstituted NC fibres are drawn from lyotropic solution.

EXPERIMENTAL

NC/THF/EtOH compositions within either the isotropic + anisotropic biphasic field in Figure 2, or in the anisotropic single-phase field, were prepared as follows: a known mass of NC was dissolved completely in sufficient THF to give a 2 vol% clear solution. The solvent was allowed to evaporate at room temperature until the mass of the solution equalled that calculated to correspond to the concentration required. Ternary compositions, i.e. those which also included

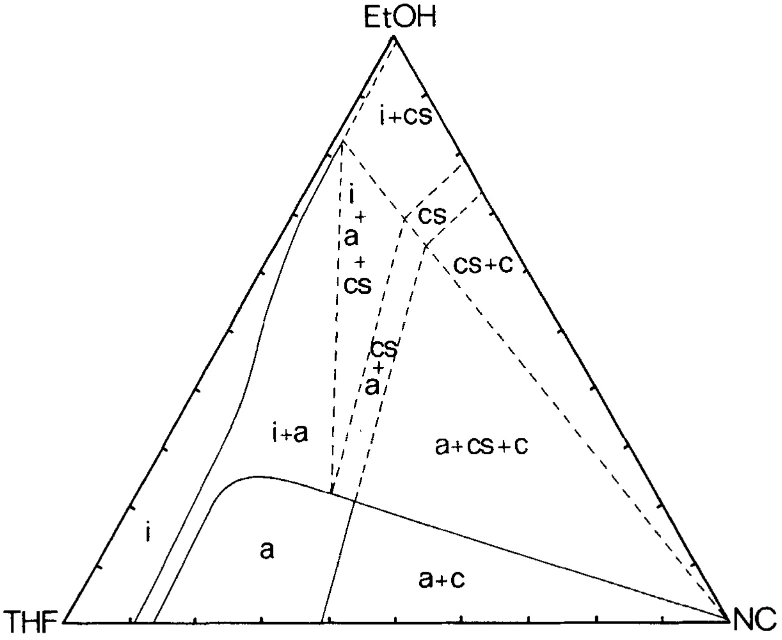

FIGURE 2 Room temperature section through the phase diagram for NC/THF/EtOH. Adapted from Ref. 13.
i = isotropic; a = anisotropic (mesophase); c = crystalline; cs = crystallosolvate.

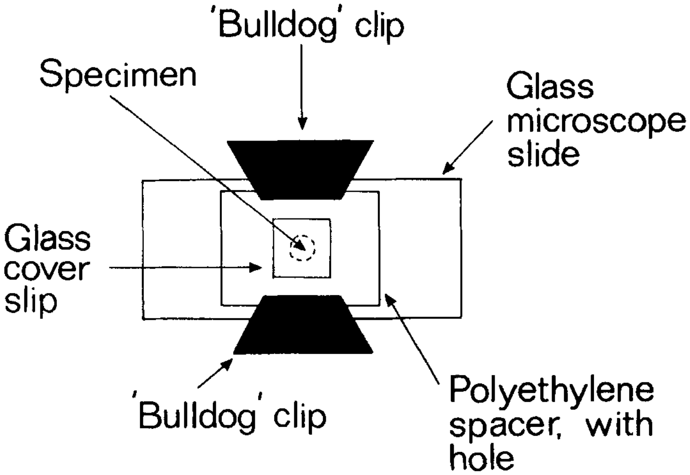

FIGURE 3 Schematic diagram of the simple cell used to minimise the loss of volatiles during microscopic observation of specimens.

non-solvent, were made by adding EtOH to a system already containing NC and THF in the required ratio. Preparations were allowed to stand for a day, prior to withdrawing samples for optical microscopy. Our stated route of specimen preparation is preferred to simply mixing the components in their final proportions, since the kinetcis of dissolution are slow for high polymer concentrations, and one cannot be certain whether equilibrium is ever attained in this case.[14]

Optical textures were observed with a Carl Zeiss (Jena) Amplival D polarising microscope. To minimise the loss of volatiles during microscopic observation, samples were held in the simple cell shown in Figure 3. The polyethylene spacer, maintained a ~10 μm gap between the glass microscope slide and cover slip. The cell is an effective container; the weight loss of volatiles, relative to the amount originally present, was never found to exceed 2.5% over a 7-day period.

Thin sheared specimens were prepared from the solutions by using a 4cm long cover slip with the containment cell; it was drawn rapidly across the solution before being secured with the building clips. The shear rate is estimated as being ~$10^4 s^{-1}$, since the cover slip was moved at ~10 cm · s^{-1} and the specimens were ~10 μm thick. Sheared specimens were examined in the polarising microscope.

Fibres of reconstituted NC were drawn from solution with the apparatus shown schematically in Figure 4. Extrusion through the die gave a reduction in area of 100:1. Both the primary and secondary draw ratios were chosen to be as high as was possible without breaking the fibre, and varied slightly with solution composition. The normal primary draw ratio, calculated from the relative speeds of ram travel and primary spool rotation (i.e. neglecting volume change due to the loss of volatiles), was typically ~1.3. The secondary draw ratio calculated from the relative speeds of primary and secondary spool rotation was also ~1.3, giving an overall draw ratio of ~1.7. The

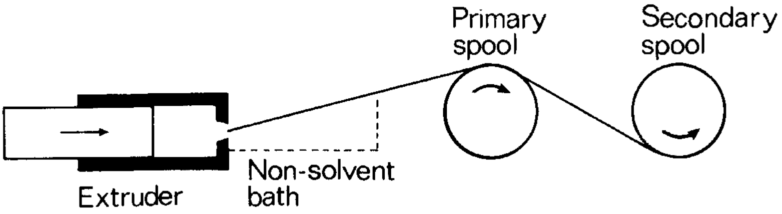

FIGURE 4 Schematic side-view of apparatus used to extrude and draw fibres of reconstituted NC from NC/THF/EtOH compositions.

nominal strain rate could be controlled by altering the distances between the die and primary spool, and between the primary and secondary spools; assuming uniform extension of the fibre between spools, it was typically $\sim 10^{-2}s^{-1}$ for both stages. The non-solvent bath was left empty when biphasic (isotropic + anisotropic) NC/THF/EtOH compositions were being drawn. However, it was filled with EtOH when the extrudate consisted of single phase (anisotropic) solutions; initially this was done to give the material reliable cohesivity during drawing.

The drawn fibre was examined in the polarising microscope, and x-ray diffraction patterns were obtained with a microbeam camera (beam diameter ~100 μm).

RESULTS AND DISCUSSION

Equilibrium Molecular Ordering

The room temperature section of the phase diagram reproduced in Figure 2 shows that the critical volume fraction for mesophase formation in NC/THF is ~0.11. Given[15] a polymer molecular weight M_n of $\sim 7 \cdot 10^4$, a molecular aspect ratio of ~200 can be estimated, assuming the molecules to be completely rigid rods. Flory's theory[10] predicts that such molecules should first form a mesophase at a volume fraction of ~0.05. Clearly, NC molecules in THF are less than rigid. Previous work on other cellulose derivatives[8,9] shows that the critical concentration is typically greater than our value for NC in THF, even for molecules with an overall aspect ratio greater than 200. (The exact value for hydroxypropyl cellulose varies between 0.28 and 0.42, depending on the solvent used.) There have been various attempts (reviewed briefly in ref. 9) to modify Flory's original theory by modelling the molecules as semi-flexible chains. Our experimental result for NC in THF suggests that this polymer belongs to the rigid end of the spectrum of semi-flexible molecules. Partial flexibility in NC can arise from (hindered) rotation about the β-linkages between rings, and also from oscillations of the "armchair" ring[16] (there being no double bonds) between the conformations shown in Figure 5.

The optical textures exhibited by the single-phase anisotropic NC/THF/EtOH compositions are typically of the nematic Schlieren type (Figure 6a), though occasionally oily streaks (Figure 6b) or Grandjean walls are seen, suggesting cholesteric ordering. We note that cellulose derivatives, like cellulose itself, are chiral, and therefore *must* be

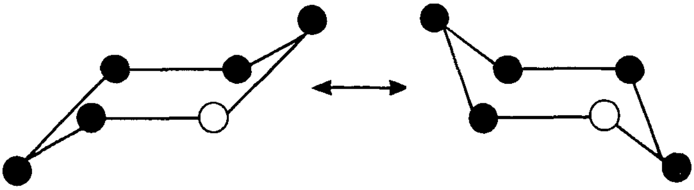

FIGURE 5 The two "armchair" conformations of a glucose residue in the cellulose chain. The open circles denote the oxygen atom in the ring.

cholesteric,[9] at least if there is a predominance of left- or right-handed molecules. However, if the pitch of the cholesteric helix is sufficiently large (as would be the case for a nearly racemic mixture), the molecular ordering may approximate to being nematic over distances corresponding to typical domain sizes in the texture. A check that the mesophase does possess an equilibrium layered structure is afforded by observing the relaxation behaviour of thin sheared films of anisotropic NC/THF/EtOH. When specimens are sheared between glass surfaces as described in the experimental section above, a banded texture, characteristic of many sheared liquid crystalline polymer systems,[17,18] is formed (Figure 7a). Within two days of shearing, the

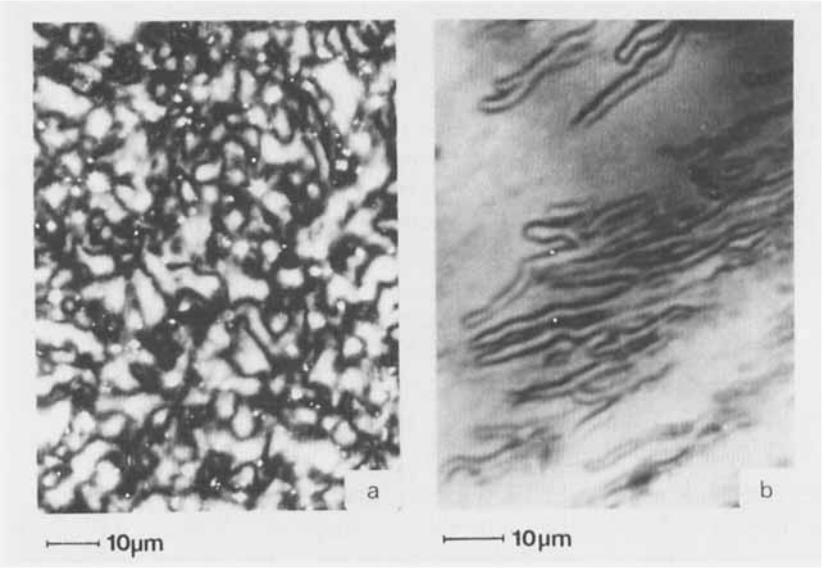

FIGURE 6 a) Schlieren texture of a single phase anisotropic NC/THF/EtOH composition.
b) Oily streak texture of a similar composition.
Crossed polars; polariser transmission direction horizontal.

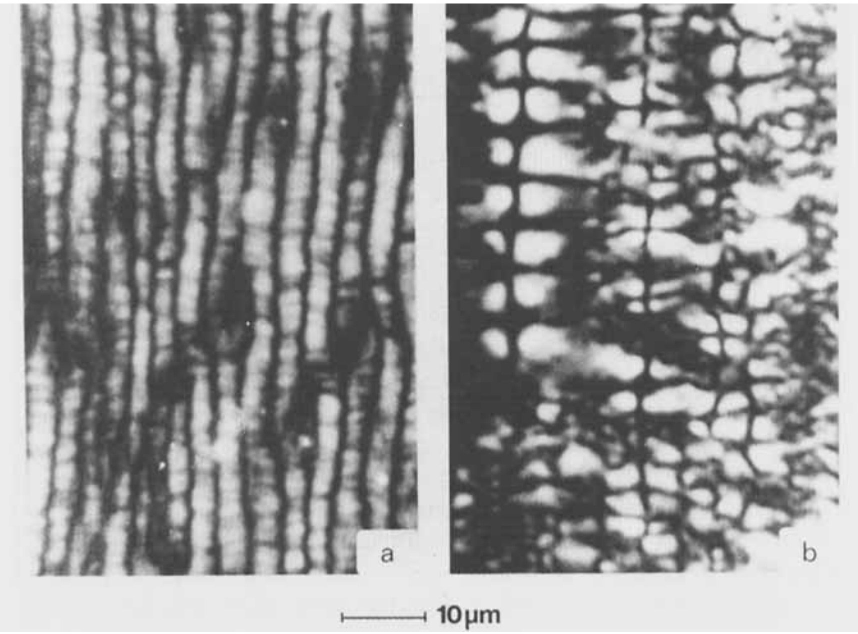

FIGURE 7 a) Banded texture in sheared single phase anisotropic NC/THF/EtOH. b) Imperfect parabolic focal conic texture in the same specimen, after two days. Crossed polars; polariser transmission direction horizontal, parallel to shear direction.

texture relaxes to that shown in Figure 7b. The rectangular grid pattern of extinction lines is similar to that formed on relaxing sheared hydroxypropyl cellulose/solvent systems.[19] As the microscope focus is altered, the behaviour of the texture follows that documented for parabolic focal conic (P.F.C.) textures.[19–22] Such textures are in turn associated with the molecules being ordered in layers.

In anticipation of the further results to be reported below, it is worth noting that a banded texture, and subsequent formation of a P.F.C. texture, is also observed after shearing biphasic (isotropic + anisotropic) NC/THF/EtOH compositions.

Drawing Reconstituted NC Fibres

On drawing, as described in the experimental section, NC/THF/EtOH compositions within the isotropic + anisotropic field on the phase diagram typically yielded reconstituted fibres having the optical microstructure shown in Figure 8a. When the fibre axis is parallel to the transmission direction of either polar, the extinction is patchy, suggesting that, although the material may be aligned locally, the

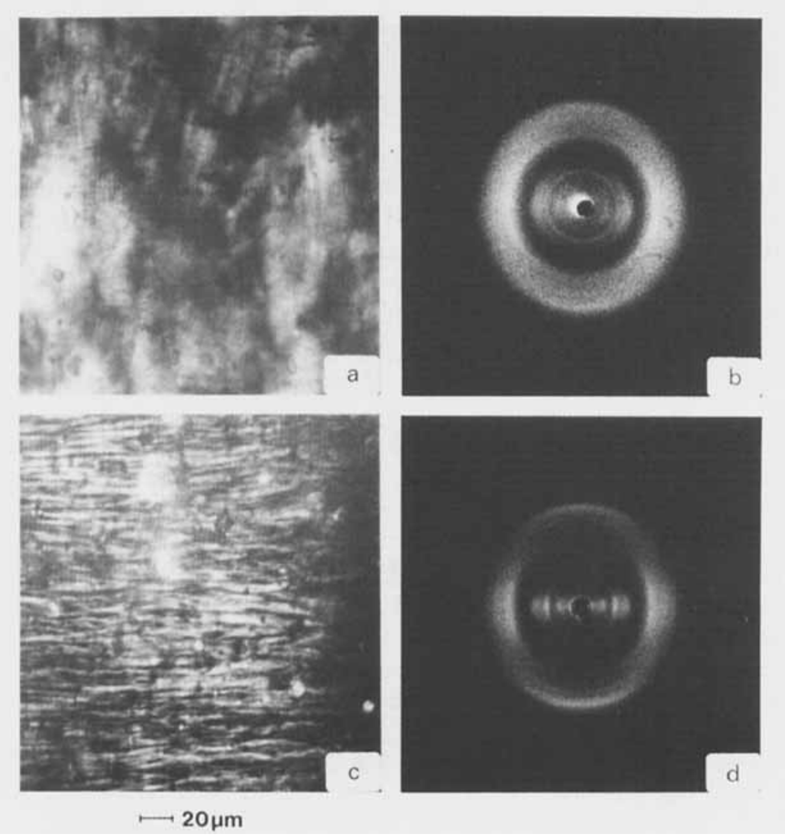

FIGURE 8 a) Optical texture of a drawn two-phase (isotropic + anisotropic) NC/THF/EtOH composition.
b) X-ray microbeam diffraction pattern of the specimen shown in (a).
c) Optical texture of a drawn single-phase (anisotropic) NC/THF/EtOH composition.
d) X-ray microbeam diffraction pattern of the specimen shown in (c).
The shear direction is vertical in all cases.
Micrographs: crossed polars; polariser transmission direction horizontal.

level of global alignment is inferior. Figure 8b reproduces the microbeam x-ray diffraction pattern of the specimen shown in Figure 8a. The extent of arcing of the equatorial maxima confirms the relatively poor level of global molecular alignment.

Figure 8c shows the optical texture typical of fibres drawn from single (anisotropic) phase NC/THF/EtOH compositions. The corresponding x-ray diffraction pattern is reproduced in Figure 8d. There are clear differences between these fibres and those drawn from the biphasic solutions:

a) The fibres have a banded texture when viewed with the fibre axis parallel to the transmission direction of either polar;

b) The degree of global molecular orientation is improved;

c) The lateral extent of regions of local ordering is increased.

Drawing fibres from a single anisotropic phase through a non-solvent bath would seem to yield fibres with the best-defined ordered structure for analysis by x-ray diffraction.

In the case of the biphasic isotropic + anisotropic compositions, we may be dealing with an example of a system in which nematic-like order can be induced in originally isotropic material by shear flow.[23] Given that the local molecular ordering associated with banded textures is compatible with that in a nematic,[18,24] this could explain why banded textures are observed after the biphasic NC/THF/EtOH compositions are sheared at $10^4 s^{-1}$ between glass slides, while they are not observed in the extruded and drawn fibres.

Fibres drawn from the biphasic compositions most likely contain a significant fraction of disordered molecules. When we draw single-phase anisotropic NC/THF/EtOH through the EtOH bath, we rely on shear flow, together with the sluggish nature of phase transformations in this system, to prevent the formation of a significant amount of isotropic phase. In any case, we regard the primary role of EtOH in this situation as one of aiding the rapid removal of THF during regeneration of the solid polymer fibre, rather than as one of replacing THF in the extrudate.

The phase diagram section shown in Figure 2 was plotted by observing microscopically the phases which formed after compositions were prepared via the same route as that used in the present paper. If the isotropic phase formed by compositions in the three-phase region is isolated, and the volatile components are allowed to evaporate from this phase, a residue having the characteristics of a crystallosolvate is formed. We have demonstrated[13] that it consists of NC/EtOH. Crystallosolates involving cellulose derivatives have previously been observed with NC/acetone,[25] and with cellulose tricarbanilate/methyl-ethyl-ketone.[26] If x-ray diffraction by the drawn fibres is to be used for conformational analysis, one has to be certain that the fibres do indeed consist entirely of reconstituted NC, and do not contain residual EtOH as a crystallosolvate. Given the form of Figure 2, the possibility exists that crystallosolvate might form as THF is lost from the extrudate in our fibre drawing process, depending on the amount of EtOH in the system. However, we have no direct way of telling what path our starting composition follows on the diagram as the fibre is drawn, or whether there is indeed sufficient time for crystallosolvate to form.

Knowing that the crystallosolvate decomposes rapidly on heating to above 150°C,[13] we heated the reconstituted fibres to above this temperature, measuring the mass of the fibre before and after this treatment. There was no detectable change in mass, so we are confident that no significant amount of crystallosolvate is formed during extrusion/drawing. As a further check for the presence of crystallosolvate, we attempted to obtain the x-ray diffraction pattern of this phase. Crystallosolvate was produced on a glass microscope slide by allowing volatiles to evaporate from the isotropic phase formed by a composition plotting in the three-phase field on the phase diagram. The crystallosolvate was removed from the glass substrate with a razor blade, and an aggregate small enough to support its own weight was held in the x-ray microbeam camera. Since the volume of specimen in the beam was small, the contribution of air scattering to the resulting diffraction pattern was significant. Images were therefore digitised, using an image processing system[27] which reads in data from the x-ray film via a scanning microdensitometer. Film was also exposed in the microbeam camera without a specimen present, allowing the air scatter to be subtracted from the previous data, and a radially averaged section through the data was plotted (Figure 9a). It was not possible to separate the original pattern into equatorial and meridional components. We also obtained a radially averaged section (Figure 9b) from the diffraction pattern of as-received NC (DS = 2.72, the fibres being too short to allow a pattern for aligned material to be recorded), and from NC which had been reprecipitated from THF solution with distilled water and then dried (Figure 9c). Finally, we used the image processor to obtain equatorial and meridional profiles through the diffraction patterns shown in Figures 8b and 8d (Figures 9d and 9e, and 9f and 9g, respectively). The indexing of peaks in the pattern for as-received polymer (Figure 9b) follows the convention of previous workers,[25,28,29] with the b-axis of the unit cell lying parallel to the chain axis; all three maxima have previously been identified on *equatorial* sections through the fibre patterns of partially nitrated cellulose. The pattern for NC reprecipitated from THF by water (Figure 9c) is similar, though no (002)-type reflection is resolved, and the real space *d*-spacings for (101) and (012) are slightly larger than for as-received polymer. The diffraction maxima in the crystallosolvate pattern occupy positions very different from those in the above two NC patterns. If we now look at the equatorial and meridional sections of the pattern from drawn biphasic NC/THF/

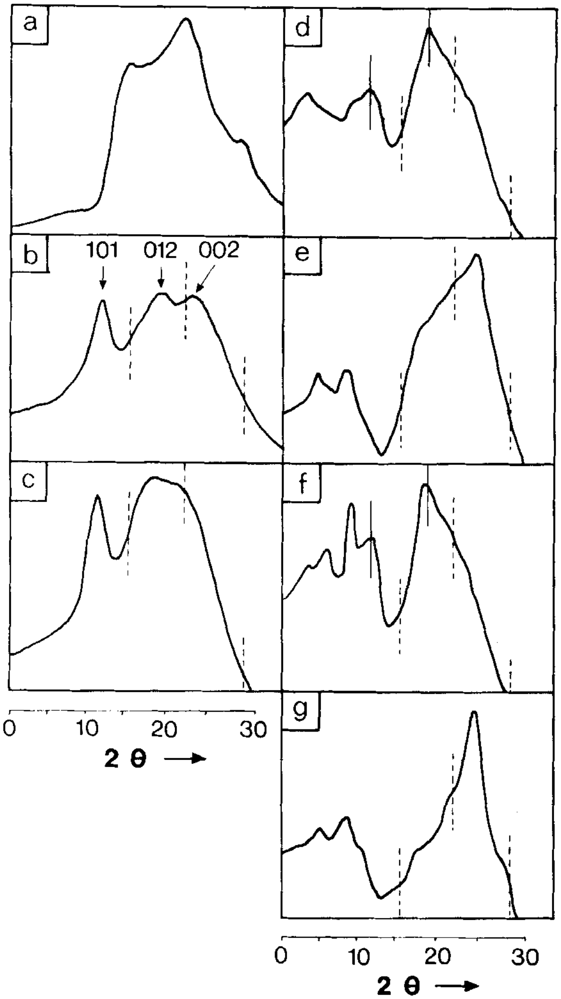

FIGURE 9 Sections through microbeam x-ray diffraction data:

a) Crystallosolvate; radially averaged section.

b) As-received NC; radially averaged section.

c) NC reprecipitated from solution in THF; radial section.

d) NC drawn from two-phase (isotropic + anisotropic) NC/THF/EtOH; equatorial section.

e) NC drawn from two-phase (isotropic + anisotropic) NC/THF/EtOH; meridional section.

f) NC drawn from single-phase (anisotropic) NC/THF/EtOH; equatorial section.

g) NC drawn from single-phase (anisotropic) NC/THF/EtOH; meridional section.

Vertical broken lines in (b)–(g) denote the positions of crystallosolvate peaks as determined from (a).

Vertical continuous lines in (d) and (f) denote the positions of (101) and (012) "equatorial" maxima as determined from (c).

EtOH, we find equatorial maxima corresponding exactly in position to the (101) and (012) type reflections of NC precipitated from THF solution by water. Some additional maxima are also seen, but none of these corresponds to any of the crystallosolvate reflections either. We find similar results for the equatorial and meridional sections of the pattern from drawn single phase NC/THF/EtOH (Figures 9f and 9g), though the additional reflections are rather sharper. There remains the possibility that *all* the crystallosolvate reflections are meridionals in the fibre pattern, so that the appropriate reciprocal lattice points do not intersect the Ewald sphere for the diffraction geometry used in the microbeam camera.[30] However, it is unlikely that *all* the rings sampled in Figure 9a arise from intramolecular scattering, and the measured diameters of the rings are not related in any simple way. Furthermore, we have obtained diffraction data from the reconstituted fibres in symmetrical transmission, which allows direct sampling of the meridian, and we found no additional maxima. The observations on the x-ray diffraction patterns reinforce our confidence that the reconstituted fibres drawn from NC/THF/EtOH do not contain a significant amount of crystallosolvate, and that the fibres will therefore be useful in structural studies of NC conformations.

Solid-state order in reconstituted NC

A striking feature of the diffraction data shown in Figures 8b and 8d is that the fibres drawn from single phase NC/THF/EtOH appear to have a high degree of lateral molecular ordering—which seems surprising in view of the fact that we are dealing with what is essentially a random copolymer. The lateral extent of ordered regions in fibres drawn from biphasic NC/THF/EtOH is somewhat smaller, and still less order is evident in the pattern of NC precipitated from THF solution by water (Figure 9c). Whether or not different chains consisting of a random sequence of monomers can contain runs which are similar and therefore propagate a crystal-like entity laterally, raises questions of a statistical nature. The problem has been investigated for molecules consisting of a random sequence of two monomer types,[31,32] leading to the concept of "non-periodic layer" (NPL) crystallites, consisting simply of laterally matched sequences of the random chains.

As a first order attempt to extend the model to NC, we started with the following simplifications:

Molecules of NC having a DS equal to 2.72 can be regarded as consisting of three monomer types, as discussed in the Introduction above. A DS of 2.72 requires a 0.72 probability of a glucose residue being nitrated in the 2,3 and 6 positions, and we assume 0.14 probabilities for 2,6-nitration and for 3,6-nitration. Assuming further that these monomer types are of equal length and randomly distributed along the chains, we "built" 100 molecules, each 100 units long, using a desk-top microcomputer. The first molecule is taken to be fixed in position. The second is placed next to the first and shifted longitudinally relative to it, until the best (i.e. the longest) match is found between the chains. The second chain is then fixed in position, the third is placed next to it, and the process is continued. In this way, a "primary match" may be propagated laterally for a distance of several chains, until a "better" (i.e. longer) match is nucleated at some other point along the current chain. A "nucleation weighting" can be introduced into the model, in recognition of the fact that a crystallite, once nucleated, will continue to propagate laterally in preference to a new NPL crystallite being nucleated somewhere else along the chain. The conditions of molecular mobility necessary to allow searching for the best match, are most likely to be met in practice if the chains are locally aligned and in a shear flow environment. The conditions approximate to our drawing of fibres from anisotropic NC/THF/EtOH compositions.

Figure 10(a-c) shows the extent of the primary matches predicted by the computer model, for nucleation weightings of 1:1, 2:1 and 5:1 respectively. The percentage of monomer units involved in the matches is 13.2%, 11.3% and 10.9% for the three cases respectively. The simple model therefore demonstrates that significant lateral order can form in a system comprised of entirely random chains. In practice, the percentage of monomer units involved in local reinforcing units could be higher than suggested by the above figures: while the primary matches may fix the relative register of neighbouring chains, smaller secondary matches between neighbouring chains can then also be identified.

CONCLUSIONS

1. Partially nitrated cellulose forms lyotropic solutions in THF. The critical concentration required for mesophase formation suggests that the polymer molecules are less than ideally rigid.

2. The equilibrium arrangement of molecules in the mesophase favours a layered structure, consistent with their chiral nature.

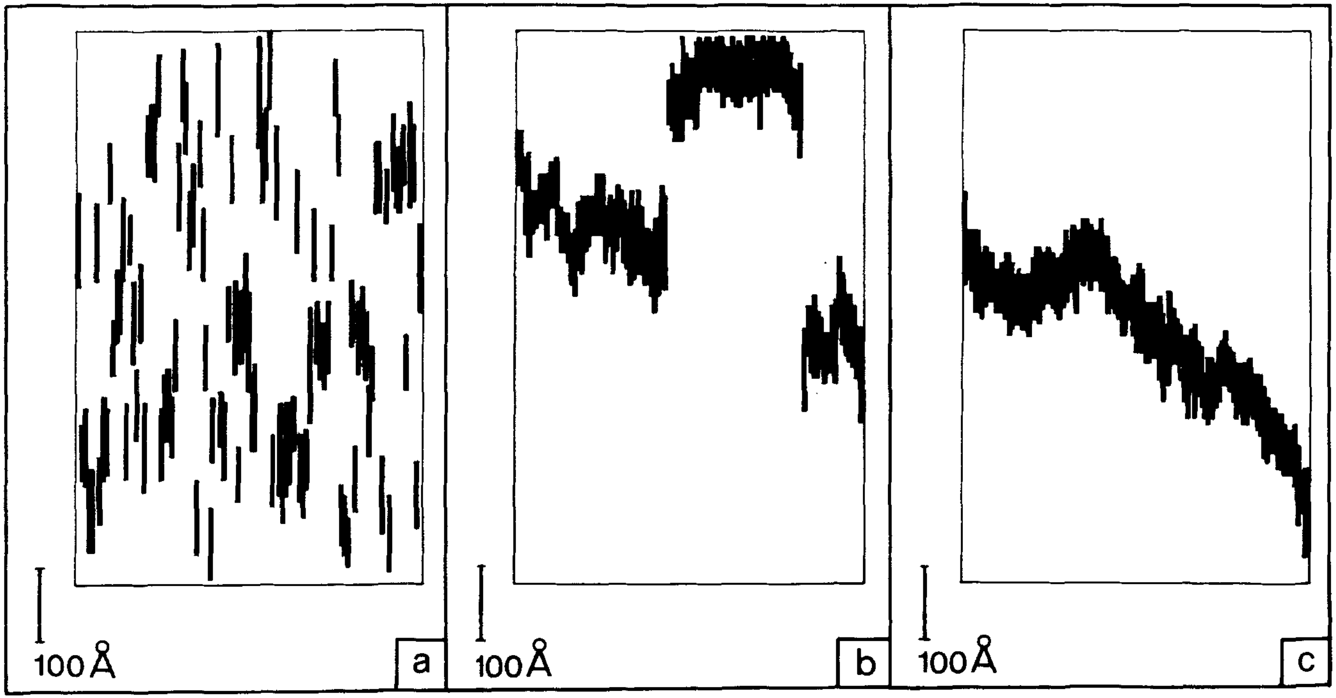

FIGURE 10 The extent of "primary matches" derived frm the computer model for NC (DS = 2.72). Each frame is 100 monomer units high and 100 chains wide.
(a) nucleation weighting 1:1; (b) nucleation weighting 2:1; (c) nucleation weighting 5:1.

3. It is possible to produce aligned reconstituted NC from single-phase anisotropic solutions or from two-phase isotropic + anisotropic solutions in THF/ethanol. In the latter case, nematic-like order may be induced in the isotropic phase by a sufficiently high shear.

4. The reconstituted material does not contain any detectable amount of crystallosolvate phase.

5. Considerable local reinforcement between chains may arise from the formation of "non-periodic layer" crystallites.

Acknowledgments

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References

1. B. P. Griffin and M. K. Cox, *The British Polymer Journal*, **12**, 147 (1980).
2. A. Ciferri, *Polymer Liquid Crystals*, Eds. A. Ciferri, W. R. Krigbaum and R. B. Meyer (Academic Press, New York, 1982), Chap. 3.
3. R. W. Lenz, *Faraday Discussions of the Chemical Society*, **79**, 21 (1985).
4. K. H. Gardner and J. Blackwell, *Biopolymers*, **13**, 1975 (1974).
5. H. Chanzy, A. Peguy, S. Chaunis and P. Monzie, *Journal of Polymer Science: Polymer Physics Edition*, **18**, 1137 (1980).
6. D. L. Patel and R. D. Gilbert, *Journal of Polymer Science: Polymer Physics Edition*, **19**, 1231 (1981).
7. E. Bianchi, A. Ciferri, G. Conio, A. Cosani and M. Terbojevich, *Macromolecules*, **18**, 646 (1985).
8. D. G. Gray, *Journal of Applied Polymer Science: Applied Polymer Symposium*, **37**, 179 (1983).
9. D. G. Gray, *Faraday Discussions of the Chemical Society*, **79**, 257 (1985).
10. P. J. Flory, *Proceedings of the Royal Society* (*London*), **A234**, 73 (1956).
11. D. T. Clark, P. J. Stephenson and F. Heatley, *Polymer*, **22**, 1112 (1981).
12. C. Viney and A. H. Windle, *Journal of Materials Science Letters*, **5**, 516 (1986).
13. C. Viney and A. H. Windle, *Liquid Crystals*, in press.
14. S. P. Papkov, *Contemporary Topics in Polymer Science*, Eds. E. M. Pearce and J. R. Schaefgen (Plenum, New York, 1977), pp. 97–108.
15. T. J. Lewis, personal communication.
16. W. T. Astbury, *Nature*, **155**, 667 (1945).
17. A. M. Donald, C. Viney and A. H. Windle, *Polymer*, **24**, 155 (1983).
18. C. Viney, A. M. Donald and A. H. Windle, *Polymer*, **26**, 870 (1985).
19. A. M. Donald and C. Viney, *Liquid Crystals*, in press.
20. C. S. Rosenblatt, R. Pindak, N. A. Clark and R. B. Meyer, *Journal de Physique*, **38**, 1105 (1977).
21. R. Ribotta and G. Durand, *Journal de Physique*, **38**, 179 (1977).
22. R. A. Asher and P. S. Pershan, *Journal de Physique*, **40**, 161 (1979).
23. D. C. Prevorsek, *Polymer Liquid Crystals*, Eds. A. Ciferri, W. R. Krigbaum and R. B. Meyer (Academic Press, New York, 1982), Chap. 12.
24. C. Viney, A. M. Donald and A. H. Windle, *Journal of Materials Science*, **18**, 1136 (1983).

25. F. D. Miles, *Cellulose Nitrate* (Oliver and Boyd, London, 1955), p. 127.
26. P. Zugenmaier and U. Vogt, *Die Makromolekulare Chemie*, **184**, 1749 (1983).
27. W. O. Saxton and T. L. Koch, *Journal of Microscopy*, **127**, 69 (1982).
28. J. Trommel, *The Nitration and the Denitration of Cellulose Nitrates II, X-ray Investigation*, Communication no. 13 from the N. V. Koninklijke Nederlandsche Springstoffenfabrieken, Amsterdam (1955).
29. J. Trommel, *The Molecular Arrangement of Cellulose Nitrates*, Communication no. 15 from the N. V. Koninklijke Nederlandsche Springstoffenfabrieken, Amsterdam (1959).
30. L. Alexander, *X-ray Diffraction Methods in Polymer Science*, (Wiley-Interscience, New York, 1969), p. 199.
31. A. H. Windle, C. Viney, R. Golombok, A. M. Donald and G. R. Mitchell, *Faraday Discussions of the Chemical Society*, **79**, 55 (1985).
32. S. Hanna and A. H. Windle, *Polymer*, in press.