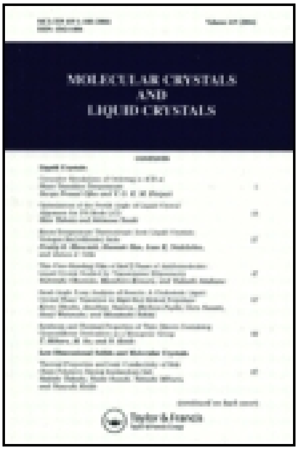

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Anisotropic Solutions of Cellulose Acetate in Trifluoroacetic Acid. Proof of Cholesteric Order by Circular Dichroism

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Anisotropic Solutions of Cellulose Acetate in Trifluoroacetic Acid. Proof of Cholesteric Order by Circular Dichroism

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Mesomorphic solutions of cellulose acetate in trifluoroacetic acid show a strong circular dichroism. This effect is related to the cholesteric structure of the solution. We have investigated the effects of change in temperature and polymer concentration. The transition from an isotropic to an anisotropic phase can be studied either directly or indirectly by the introduction of an achiral dye into the solution.

Les solutions mesomorphes d' acétate de cellulose dans l'acide trifluoroacétique présentent un fort dichroïsme circulaire. Cet effet est reliè à la structure cholestérique de la solution. Nous nous sommes intéressés aux effets de la température et de la concentration en polymere. La transition d'une phase isotrope à une phase anisotrope peut etre étudiée soit directement ou indirectement par l'introduction d'un dye achiral dans la solution.

Many semi-rigid polymers form mesomorphic solutions. These include synthetic polypeptides,[1-3] aromatic polyamides,[3-7] nucloic acids, collagen,[8-9] and more recently, this list has been extended to cellulose derivatives[10-13] and polyisocyanates.[14-16] The type of mesophase formed depends on the symmetry of the molecular interactions. For example, achiral systems such as aromatic polyamides form nematic phases, whereas chiral systems such as the polypeptides form a cholesteric phase. The only study, of which we are aware, which has attempted to characterize the mesomorphic phase for cellulose derivatives was that of Gray on the hydroxypropylcellulose/water system.[17-18]

Here, we describe the study of solutions of cellulose acetate (CA) in trifluoroacetic acid (TFA). Our previous studies of these solutions by polarizing microscopy and differential scanning calorimetry[11-12] indicated the appearance of an anisotropic phase. The concentration at which this appears depends on the temperature and molecular mass of the polymer and is in qualitative agreement with theoretical predictions.[19-20] The textures observed using an optical microscope with crossed polarizers are similar to those formed by the cholesteric phases of small molecules.[22]

We have confirmed the presence of a helicoidal structure by measurement of the circular dichroism and we have investigated the effects of temperature and polymer concentration. The rate of development of the birefringent mesophase has also been studied. We have shown that when achiral dye molecules are dissolved in this mesophase they take up the local molecular orientation just as they do when dissolved in one component thermotropic cholesteric systems[23-25] (where we are dealing with small molecules). The systems formed have strong circular dichroism in the frequency band corresponding to the absorption of the dye molecule.

SAMPLE CHARACTERISTICS AND DESCRIPTIONS OF APPARATUS

The cellulose acetate (Eastman 4655) samples contain 39.4% ± 0.5% acetyl. The ASTM viscosity is 45 ± 6 s. The average molecular mass is Mw ~ 56000.

The circular dichroism spectra were obtained with a dichrograph III CNRS Roussel Jouan-Jobin Yvon at the ISIN Laboratory of Spectroscopy and Molecular Structure, Nancy Vandoeuvre. The sensitivity of this instrument ranges from 1×10^{-6} to 2×10^{-4} at 300 nm to 800 nm. The absorption spectra of the dye in the ultraviolet-visible light range were obtained with a Jobin Yvon Duospac 203 spectrograph.

The chirality measurements for the cholesteric samples were made from 10° to 50°C. The overall variations in the absorption spectra were less than 1%. Because of the very high signal intensity, we used a sample of 0.02 nm thickness held between two glass plates.

RESULTS

The phase diagram shown in Figure 1 was determined by differential scanning calorimetry[11] (DSC) and polarization microscopy.

On the left side of the diagram at low polymer concentrations, the solution is isotropic. On the right side, the solutions are birefringent.

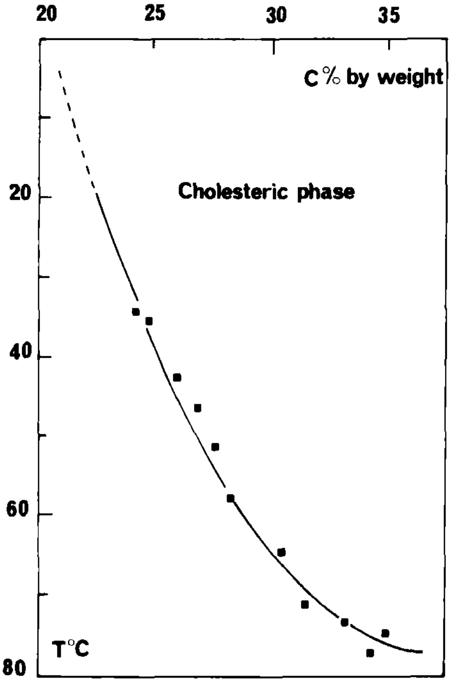

FIGURE 1 Concentration-temperature phase diagram for a cellulose acetate (CA)/trifluoroacetic acid (TFA) mixture. Molecular weight of CA ~ 56000.

The endothermal DSC peak associated with the phase transition was observed over a range of 15°C. The experimental points on this phase diagram were obtained by heating a birefringent solution of a given concentration and they correspond to the onset of the DSC peak.

The measurements of circular dichroism were made in the vicinity and on either side of the phase transition. We found that an isotropic solution does not show a dichroism signal even at a relatively high concentrations (20% at 25°C). In an anisotropic solution a strong peak is observed around 650 to 700 nm (positive cotton effect). At a given temperature, the intensity and wave length of the peak increase rapidly with time after the preparation of the sample, and stabilize after approximately one hour.

In view of the extremely high viscosity of the solution,[26] it would appear that this delay is due to the slow relaxation of internal constraints within the sample. The rate of development of the birefringent phase is shown in Figure 2 for a solution of 25% by weight of CA in TFA. As the temperature is raised, the wave length of the signal increases (Figure 3). Therefore, the length of the pitch of the cholesteric structure (where $\lambda = np$, and n is the refractive index[3,27]) also increases with temperature in contrast with the general observations on cholesterics formed by small molecules.[28] It is possible that in the

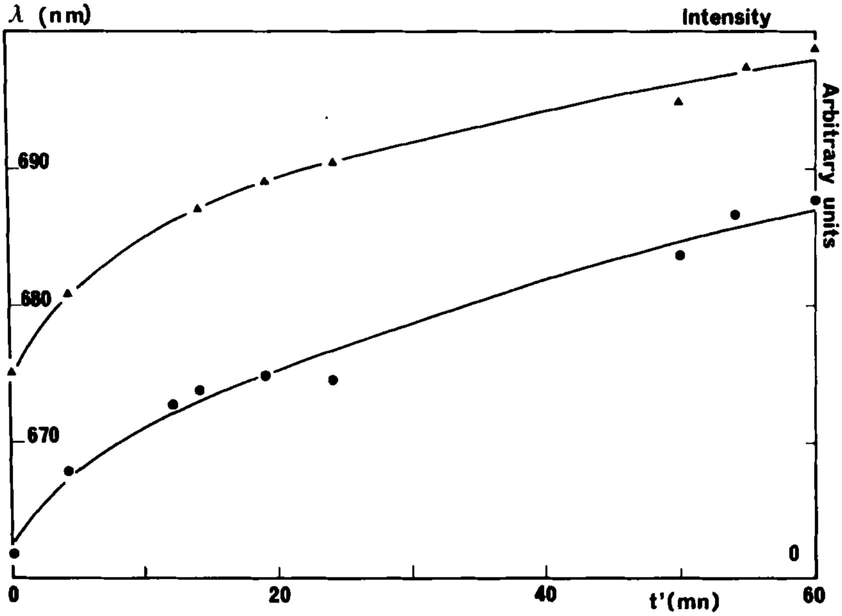

FIGURE 2 Temporal evolution of the intensity and wave length of the absorption band for anisotropic phase of a 25% by weight CA/TFA; ▲ intensity of the absorption band (Molecular extinction); ● wave length of the absorption band.

latter case, anharmonic effects are weak and lead to a release of structure at higher temperatures. On raising the temperature at a given concentration, the solution passes from the birefringent to the isotropic state and we observe a decrease in the intensity of the circular dichroism band as is shown in Figure 4.

The same experiment can be performed with the addition of a small amount of an achiral dye with an absorption band within the studied range of wavelength. Intense circular dichroism is observed in the absorption band of the dye molecules as they take up the helicoidal arrangement within the cholesteric phase.

Figure 5 shows the absorption of acridine orange dissolved in a solution of 23% CA in TFA as a function of temperature.

CONCLUSION

Circular dichroism studies indicate the presence of helicoidal order in mesomorphic solutions of cellulose acetate in TFA, proving that the phase is cholesteric. The transition from an isotropic to an anisotropic phase can be studied as a function of temperature either directly, or indirectly by the introduction of a dye into the solution. A detailed study of the effects of varying

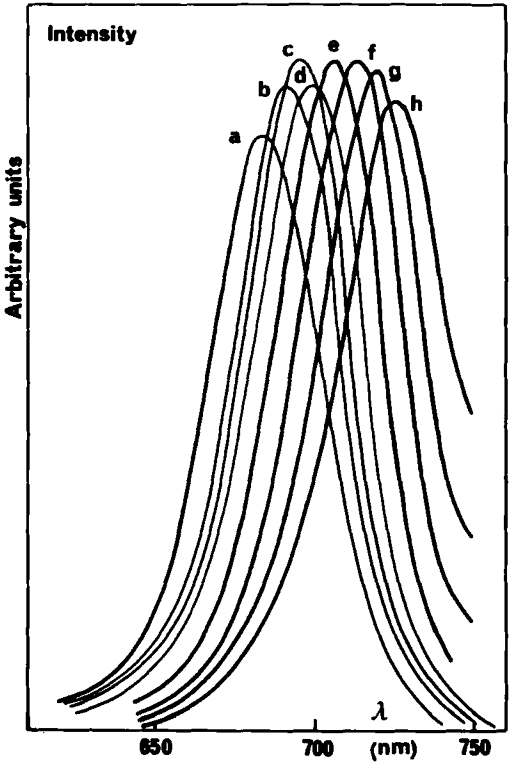

FIGURE 3 Circular dichroism peak as a function of temperature for a mixture of CA/TFA. Concentration of CA = 27% by weight; a = 35.3°C; b = 36°C; c = 37°C; d = 38°C; e = 39°C; f = 41°C; g = 42°C; h = 43°C.

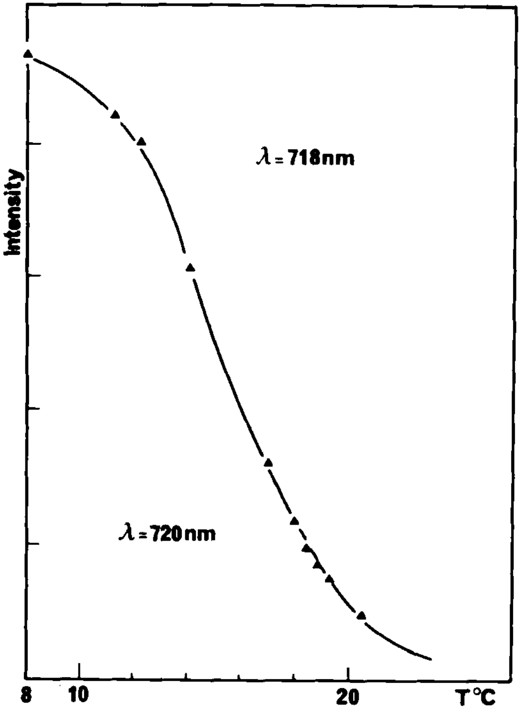

FIGURE 4 Variation of the circular dichroism intensity as a function of temperature for a solution of CA/TFA. Concentration of CA = 21% (by weight). The values given in the figure indicate the peak frequency (measurement by molecular extinction).

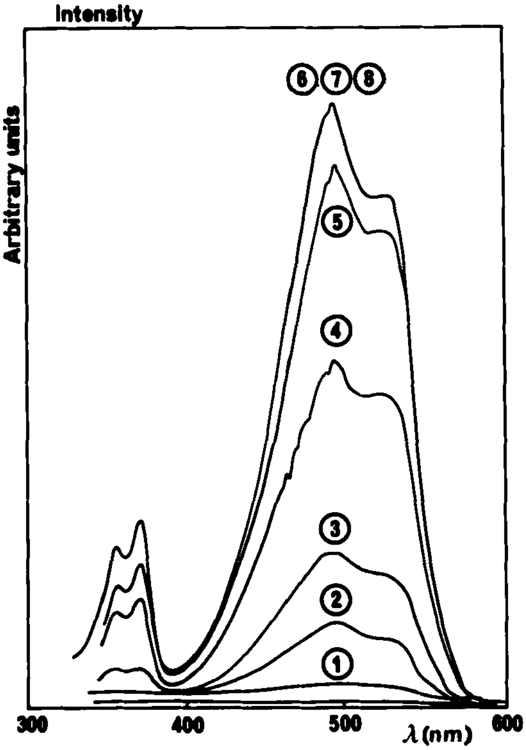

FIGURE 5 Variation of the intensity of the acridine orange absorption band as a function of temperature for a 23% (by weight) solution of CA in TFA (measurement by molecular extinction); 1 = 48°C; 2 = 43°C; 3 = 39°C; 4 = 35°C; 5 = 29.4°C; 6 = 25°C; 7 = 19°C; 8 = 13.5°C.

substituents, solvent, degree of polymerization, and substitution will be published elsewhere.[29]

References

1. C. Robinson, J. C. Ward and S. RB Beevers, *Discuss. Faraday Soc.*, **25**, 29 (1958).
2. E. T. Samulski, "*Liquid Crystalline Order In Polypeptides*" in "*Liquid Crystalline Order in Polymers,*" edited by A. Blumstein, Academic Press Inc, New York (1978).
3. N. H. Hartshorne in Liquid Crystals and Plastic Crystals, edited by G. W. Gray and P. A. Winson (Ellis Horwood, Chichester), vol 2, p. 24 (1974).
4. S. L. Kwolek, *Brevet Dupont de Nemours,* **2010,** 753 (1968).
5. M. Arpin, Thèse Strasbourg (1979).
6. B. Millaud, Thèse Strasbourg (1979).
7. M. Panar, L. F. Beste, *Macromolecules,* **10,** 1401 (1977).
8. C. Robinson, *Mol. Cryst.*, **1,** 467 (1966).
9. J. Dlugosz, L. J. Gathercole and A. Keller, *Micron.*, **10,** 81 (1979).
10. M. Panar and O. B. Wilcox, *Fr. Pat.*, **77,** 03473 (1977).

11. P. Navard, S. Dayan, J. M. Haudin and P. Sixou, *J. Polym. Sci.*, in press.
12. S. Dayan, P. Sixou, P. Navard and J. M. Haudin, 11th Euro-Physics Macromolecular Physics Conference. *Properties of oriented polymers,* Leeds, April, 1981.
13. S. M. Aharoni, *Mol. Cryst. Liq. Cryst.*, **56,** 237 (1980).
14. S. M. Aharoni, *Macromolecules,* **12,** 94 (1979).
15. S. M. Aharoni, *J. Polymer Sci.*, **18,** 1303 (1980).
16. S. M. Aharoni, *J. Polymer Sci., Polymer Lett.*, **17,** 321 (1979).
17. R. R. Werbowyj and D. G. Gray, *Mol. Cryst. Liq. Cryst.*, **34,** 97 (1976).
18. R. S. Werbowyj and D. G. Gray, *Polymer Preprints,* **20,** 102 (1979).
19. P. J. Flory, *Proc. Roy. Soc.* (*London*), **A234,** 60 (1956).
20. P. J. Flory, *Proc. Roy. Soc.* (*London*), **A234,** 73 (1956).
21. P. Pincus and P. G. De Gennes, *J. Polym. Sci. Polym. Symp.*, **65,** 85 (1978).
22. H. Kelker and K. Hatz, "*Handbook of Liquid Crystals,*" Verlag Chemie, Weinheim (1980).
23. F. D. Saeva and J. J. Wysocki, *J. Amer. Chem. Soc.*, **93,** 5928 (1971).
24. F. D. Saeva, *J. Amer. Chem. Soc.*, **94,** 5135 (1972).
25. N. Tsuchihashi, H. Nomori, M. Hatano and S. Mori, *Bull. Chem. Soc. Japan,* **48,** 29 (1975).
26. S. Dayan and P. Sixou, in preparation.
27. M. L. De Vries, *Acta Cryst.*, **4,** 219 (1951).
28. P. N. Keating, *Mol. Cryst. Liq. Cryst.*, **8,** 315 (1969).
29. J. Lematre, S. Dayan and P. Sixou, in preparation.