Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Circular Dichroism of Cholesteric Cellulose Acetate Solutions; Dependence on Molecular Weight

P. Sixou [a] , J. Lematre [a] [b] , A. Ten Bosch [a] , J. M. Gilli [a] & S. Dayan [a]

[a] equipe Dynamique des Milieux Organises Laboratoire de Physique de la Matiere Condensee, Laboratoire associe au CNRS No 190, Universite de Nice, Parc Valrose, 06034, Nice, CEDEX, France

[b] Faculté des Sciences Pharmaceutiques et Biologiques, S. Rue Albert Lebrun, B. P. 403, 54001, Nancy, France

Version of record first published: 28 Mar 2007.

To cite this article: P. Sixou , J. Lematre , A. Ten Bosch , J. M. Gilli & S. Dayan (1983): The Circular Dichroism of Cholesteric Cellulose Acetate Solutions; Dependence on Molecular Weight, Molecular Crystals and Liquid Crystals, 91:3-4, 277-283

To link to this article: http://dx.doi.org/10.1080/00268948308083689

Mol. Cryst. Liq. Cryst., 1983, Vol. 91, pp. 277–283
0026-8941/83/9104–0277/$18.50/0

Printed in the United States of America

The Circular Dichroism of Cholesteric Cellulose Acetate Solutions; Dependence on Molecular Weight

P. SIXOU, J. LEMATRE,[†] A. TEN BOSCH, J. M. GILLI, S. DAYAN

equipe Dynamique des Milieux Organises Laboratoire de Physique de la Matiere Condensee, Laboratoire associe au CNRS No 190, Universite de Nice, Parc Valrose 06034 Nice CEDEX France

(Received May 17, 1982; in final form September 20, 1982)

Concentrated solutions of cellulose acetate in trifluoroacetic acid are cholesteric liquid crystals. The circular dichroism of solutions of two samples of cellulose acetate of different molecular weights has been examined. We found that under the same conditions of temperature and polymer concentration by weights the solutions of the higher molecular weight polymer gave circular dichroism peaks at higher wavelength and of higher intensity and are presumably more highly ordered. Solutions containing mixtures of polymer chains of two different lengths gave a single circular dichroism peak which occurred at a wavelength intermediate between those corresponding to the two polymer species. The intensity of the peak was, however, considerably reduced, in some instances being lower than that which would have been given by either component taken on its own.

INTRODUCTION

It is now well established that concentrated solutions of cellulose derivatives form mesophases.[1–12] The threshold concentration for the formation of these mesophases depends on various parameters such as the polymer chain length, the nature and degree of substitution, the temperature and the nature of the solvent. For hydroxypropyl derivatives and for acetate derivatives it has been found that the mesophase is cholesteric. In previous investigations we have studied solutions of cellulose acetate (CA) in trifluoroacetic acid (TFA). Several experimental techniques were employed: polarization microscopy, differential scanning calorimetry, viscometry and circular

---

[†] Faculté des Sciences Pharmaceutiques et Biologiques, S. Rue Albert Lebrun, B. P. 403, 54001 Nancy France.

dichroism measurements (CD); the effects of changes in temperature, solvent and molecular weight on the phase transitions have been previously reported.[12] In particular it was found that the shorter the polymer chain the higher the threshold concentration required for the appearance of the mesophase.

This investigation extends the studies and was carried out to explore the influence of molecular weight on the cholesteric structure of CA/TFA solutions.

EXPERIMENTAL

Single component solutions: The apparatus and experimental procedure used have been described previously.[12] Two CA samples were investigated with molecular weights 56,000 and 30,300. These samples had the same degree of substitution and to make comparison possible, all of the solutions used contained the same concentration of polymer; 25% by weight.

We found (see Table I and Figures 1 to 3) that there is a progressive increase in both the intensity of the CD band and its wavelength after preparation of the sample. For both quantities, the maximum value was attained after about 30 minutes. We interpret these effects in terms of the relaxation of internal constraints within the sample and this would be expected to be relatively slow because of the high viscosity of the material. At room temperature the solutions degrade after one or two days and they must therefore be kept at low temperatures.

As expected we observed (Figure 4) a displacement of the temperature of the isotropic → cholesteric transition T_t. This temperature was about 30.5°C for the 30,300 Dalton sample and about 37°C for the 56,000 sample. The definition of T_t is somewhat arbitrary because the intensity of the dichroism band did not fall abruptly at a particular temperature but steadily decreased over a temperature range of 10–15 degrees. In this work we chose for T_t the temperature where the intensity of the CD peak had

Table I

M	56000	¾ 56000 ¼ 30300	½ 56000 ½ 30300	¼ 56000 ¾ 30300	30300
I_{max}*	3500 4300	2140 2460	1240	220 230	1900
λ_{mean}	690	680	660	650	600
T_t	37	29.5	28.5	28.5	30.5

*We indicate the maximum and minimum values observed from different experiments.

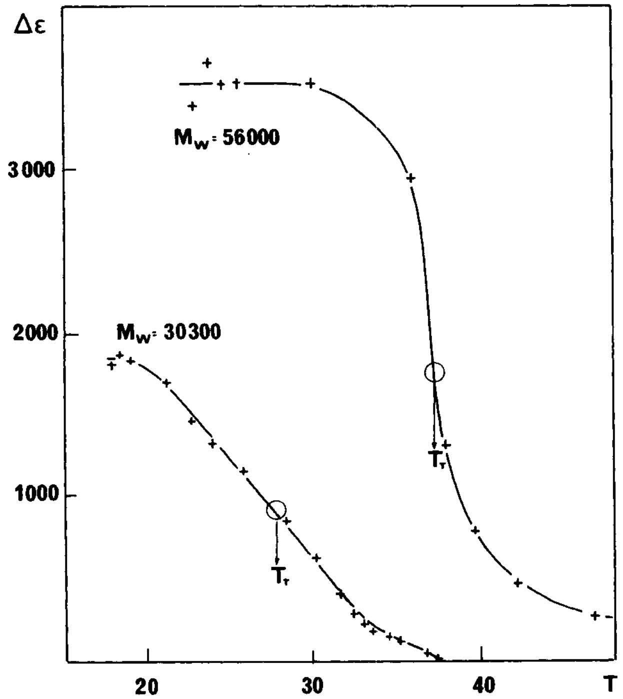

FIGURE 1 Intensity of circular dichroïsm peaks as a function of temperature; $\Delta\varepsilon = \varepsilon_L - \varepsilon_R$ (for two molecular weights) is in litres · moles^{-1} · cm^{-1}.

fallen to half of the maximum value but our qualitative discussion below would not have been altered if T_t had been taken as the temperature of the onset of dichroism.

Mixed solutions: Three mixed solutions were prepared containing 25/75, 50/50 and 75/25 ratios of the two CA samples. As in the single solute studies, a total polymer concentration of 25% by weight was used.

We found that these mixed solutions gave single CD peaks with a wavelength lying between those corresponding to the separate components and closer to the wavelength of the component in excess. The peaks were broader than for the single component solutions. It is not easy to give a quantitative estimate of peak width because of the non-gaussian shape, but it was clear that the broadening was most noticeable for the 25/75 mixture with excess of the 56,000 Dalton sample. There is also a drastic reduction in the peak height and this may be so pronounced that the intensity of the

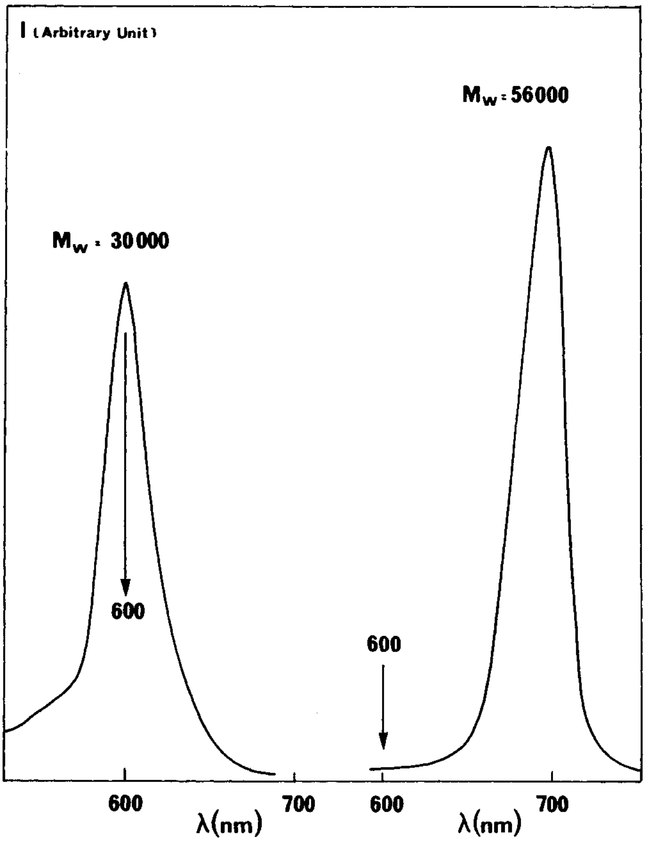

FIGURE 2 Shape of dichroïsm peak for solutions of one chain length in TFA (25% by weight).

peak is less than that corresponding to either of the two components alone. It also appears that the transition temperature T_t is reduced, but again it is not easy to give a quantitative assessment of this effect because of the gradual nature of the thermal transition.

DISCUSSION

The wavelength of the CD peak is a direct measure of the pitch, P, of a cholesteric structure $\lambda = Pn$ where n is the refractive index.

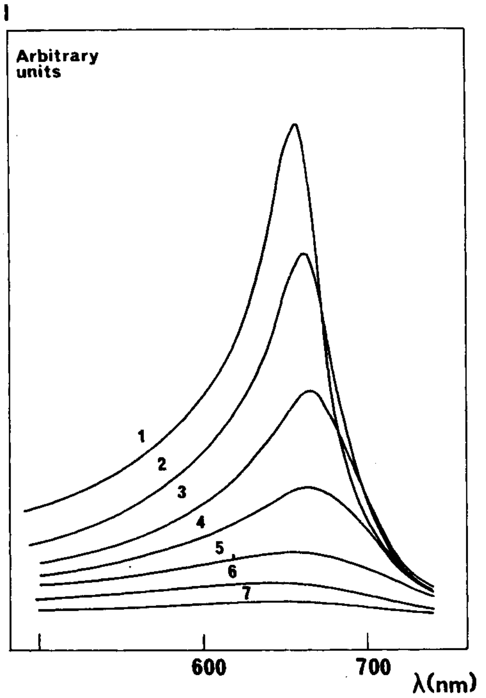

FIGURE 3 Shape of dichroïsm peak for solutions of a mixture of polymers (¾ of 30300 and ¼ of 56000) in TFA (25% by weight). (1) = 22.2°C (2) = 26.2°C (3) = 28.6°C (4) = 30°C (5) = 31.2°C (6) = 32.8°C (7) = 34°C.

A theory for the cholesteric phase of small molecules has been proposed by Goossens.[13] This is based on a minimization of the dispersive energies arising from dipole/quadrupole interactions. The same approach was later adopted by Samulski for the case of solutions of helical rod-like macromolecules.[14] According to this theory the helicoidal structure should unwind as the polymer rods increase in length. Our observations of the increase of CD peak wavelength with polymer molecular weight are in agreement with this. Previous investigations of cholesteric solutions of poly-γ-benzyl-L-glutamate have, however, not given results which are in accordance with the theory. Robinson found no variation of pitch with molecular weight[15] (although his samples may have been too polydisperse for the effect to be discernible), and Duke and Dupré actually found a decrease of pitch with increasing molecular weight.[16]

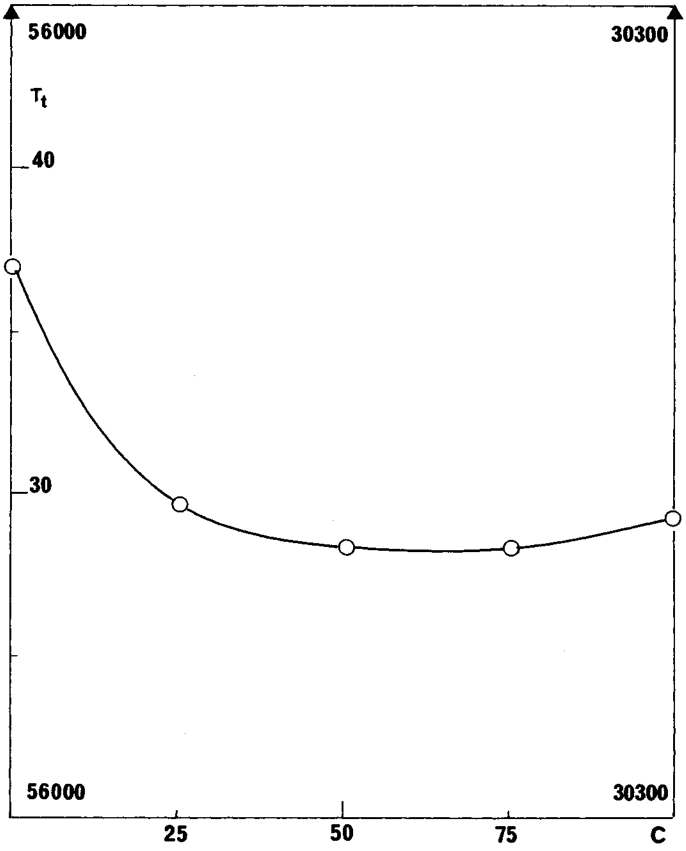

FIGURE 4 Temperature T_t as a function of concentration.

The fall in T_t as the molecular weight decreases is in agreement with the phase diagram determined previously and is in accordance with both the Flory theory[17,18] and the mean field theory for solutions of semi-rigid chain molecules.[19] Similarly the variation of peak intensity with molecular weight is as one would expect. The intensity is related to the degree of order of the sample. We expect, at a given temperature, the solutions of longer molecules (which have a higher T_t) to be more ordered than the solutions of shorter molecules.

The fact that the mixtures showed only one CD peak indicates that there is mixing at a molecular level and we are not dealing with two-phase systems. However, the broadening and decrease in intensity of the peaks indicates that the mixtures are far from ideal and are less ordered than single component solutions. This is in agreement with the observation that a decrease in CD peak height is accompanied by a decrease in transition temperature.

A more detailed investigation of polymer mixtures is in progress in our laboratory and will be presented later.

References

1. R. S. Werbowyj and D. G. Gray, *Mol. Cryst. Liq. Cryst.*, **34**, 97 (1976).
2. R. S. Werbowyj and D. G. Gray, *Polymer Preprints*, **20**, 102 (1979).
3. R. S. Werbowyj and D. G. Gray, *Macromolecules*, **13**, 69 (1980).
4. M. Panar and O. B. Wilcox, *French patent*, 770, 3473 (1977).
5. S. M. Aharoni, *Mol. Cryst. Liq. Cryst.*, **56**, 237 (1980).
6. H. Chanzy, P. Peguy, S. Chaunis, and P. Monzie, *J. Polym. Sci.*, **18**, 1137 (1980).
7. T. Tsutsui and R. Tanaka, *Polymer J.*, **12**, 473 (1980).
8. Y. Onogi, J. White, and J. Fellers, *J. Polym. Sci. Polym. Phys. Ed.* **18**, 663 (1980).
9. A. Auerbach, J. Dyer, and R. T. Vigin, *Polymer Liquid Crystal Science and Technology*, Santa Margherita (May 1981).
10. P. Navard, S. Dayan, P. Sixou, and J. M. Haudin, *J. Polym. Sci. Polym. Lett. Ed.* **19**, 379 (1981).
11. S. Dayan, P. Maissa, M. J. Vellutini, and P. Sixou, *J. Polym. Sci.* **20**, 33 (1982).
12. J. Lematre, S. Dayan, and P. Sixou, *Mol. Cryst. Liq. Cryst.*, **84**, 267 (1982).
13. W. J. A. Goossens, *Mol. Cryst. Liq. Cryst.*, **12**, 237 (1971).
14. T. V. Samulski and E. T. Samulski, *J. Chem. Phys.*, **67**, 844 (1977).
15. C. Robinson, R. D. Ward, and R. B. Beevers, *Disc. Faraday Soc.*, **25**, 29 (1958).
16. R. W. Duke and D. B. Dupré, *J. Chem. Phys.*, **63**, 143 (1976).
17. P. J. Flory, *Proc. Roy. Soc. London Ser. A*, **234**, 60 (1956).
18. P. J. Flory, *Proc. Roy. Soc. London Ser. A*, **234**, 73 (1956).
19. A. Ten Bosch, P. Maissa, and P. Sixou, Submitted to *J. Chem. Phys.*