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LONG PERIODS IN CHOLESTERYL ETHYL CARBONATE

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The various properties exhibited by liquid crystals are associated not only with the chemical composition of the molecular chains but also to a great extent with their structural characteristics. A systematic study of the molecular structure in the crystalline state for the mesogenic materials provides us with a deeper understanding on the nature of the transitions into the liquid crystalline state. In view of this, a low angle X-ray diffraction study of cholesteryl ethyl carbonate was made. This exhibits scattering curve features which closely resemble the curves of ordered semi-crystalline polymers, the characteristic features of which are the existence of long periods. The compound in the solid state consists of amorphous and crystalline components, the number and size of which are approximately equal.

1. *Introduction*

The study of liquid crystal forming materials has become very important in recent years due to their wide variety of applications. The derivatives of cholesterol which generally exhibit a cholesteric liquid crystalline phase have wide applications in medicine and technology. In particular, the straight chain alkyl esters of cholesterol occur in arterial fatty deposits and a knowledge of the crystalline forms and mesophases of these compounds may explain the conditions for the formation of these deposits and ultimately lead to preventative measures [1–4]. The various properties exhibited by liquid crystals are associated not only with the chemical composition of the molecular chains but also to a large extent with their structural characteristics. A systematic study of the molecular structure in the crystalline state for the mesogenic materials provides us with a deeper understanding of the nature of the transitions into the liquid crystalline state, as well as their physical properties [5–11], this in turn will enable us to select or modify the molecular structure to suit our requirements. In view of this, a project has been undertaken to determine the crystal structures of a series of mesogenic materials. As a part of this project low angle X-ray diffraction studies also have been undertaken. In an earlier paper we have studied cholesteryl methyl carbonate [12], which shows the existence of the long periods. Here,

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we extend the study to cholesteryl ethyl carbonate in the solid crystalline phase. This investigation is quite useful as it enables us to determine and describe the nature of submicroscopic inhomogeneities of the substance.

2. *Experimental*

The mesogenic material cholesteryl ethyl carbonate was purchased from Eastman Kodak Company, USA. This compound melts into the liquid crystalline state at 83°C and into an isotropic liquid at 105°C. The structural formula of the material is shown in Fig. 1. The samples for X-ray study were prepared in the following way. Powdered solid-crystalline cholesteryl ethyl carbonate was melted and the isotropic melt was poured into a metallic annular ring on either side of which were mica windows. After crystallization these were placed in the low angle X-ray scattering camera. The low angle scattering photographs were obtained using Indu X-ray films in a Rigaku Denki LASG6 installation with point collimation using CuK$_\alpha$ radiation with a nickel filter. The annular ring itself could be heated to any temperature by heating coils and the rate of cooling could be controlled. This arrangement was used to determine whether the rate of cooling had any effect on the specimen.

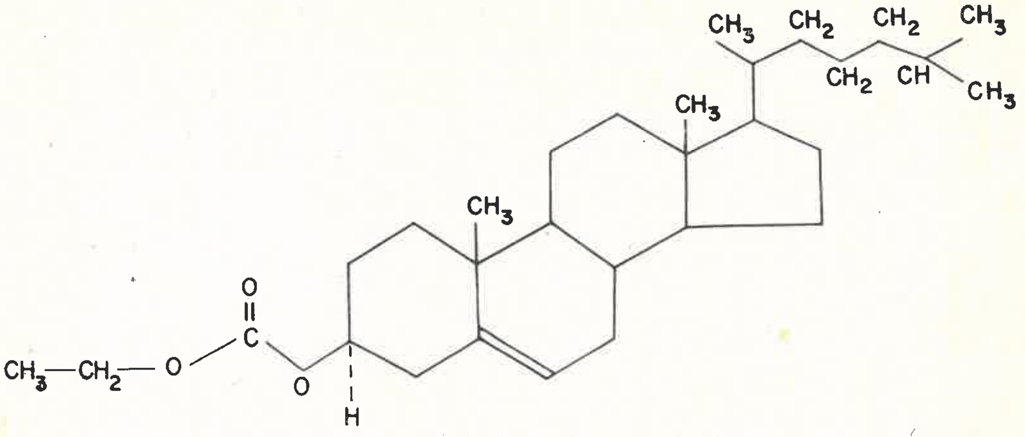

Fig. 1. Cholesteryl ethyl carbonate molecule

The geometrical optical system used by us is shown in Fig. 2. The space between the specimen and photographic cassette is used as vacuum X-ray path in the form of coaxial telescopic cylinders. Evacuation was made possible by covering the X-ray passages with myler sheets. The optical system must be set to obtain maximum intensity under the given resolving power. The vacuum X-ray path is obtained with a rotary pump and evacuating to about 10^{-1} mm Hg. The incident beam has to be intercepted. In this case, the width or the diameter of the stopper must be the same size of or larger than that of the incident X-ray beam. The diameter of the stopper *(a)* can be related to the diameter, *p*, of the first collimator, diameter, *r*, of the second collimator, the distance between first and second collimator, v, and the distance between the second collimator and the film, s, by

$$a = r + \frac{s}{v}(p+r).$$

In our geometry, we have used the following values:

$v = s = 300$ mm, $p = 0.5$ mm, $r = 0.3$ mm, "a" will become 1.1 mm.

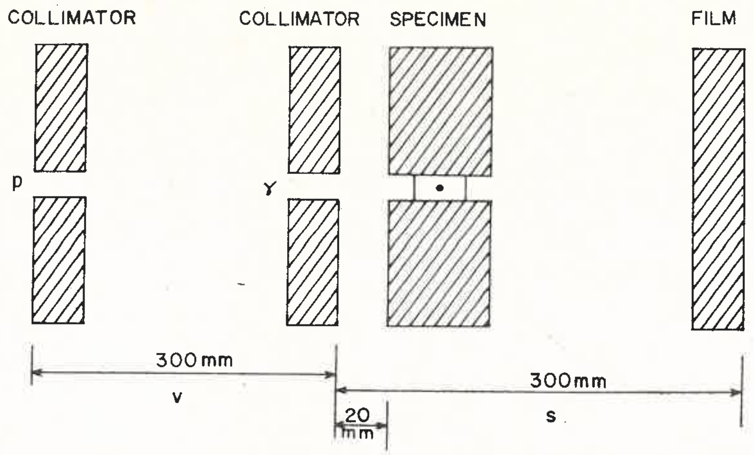

Fig. 2. The geometrical optical system used for the photographic technique

The angular characteristics of the diffraction patterns that were recorded on the film were evaluated using a Carl Zeiss-Jena GII and GIII microdensitometer and potentiometric recorder.

3. *Results and discussion*

Figure 3 illustrates the intensity distribution of low angle scattering evaluated from the photographs. The diffraction data of the molecules represents a superposition of a continuous curve due to an amorphous phase and a peak corresponding to the molecules aligned in a crystalline array. This suggests that a certain proportion of the crystallities occur in the oriented state. The shape of the scattering curve for the solid crystalline cholesteryl ethyl carbonate is in general equivalent to the intensity curves of oriented amorphous crystalline polymers, a characteristic feature of which is the existence of a long period. The long period is directly associated with density heterogeneity, the latter being due to the alternation of amorphous and crystalline regions. Many experimental investigations have been carried out in connection with long periods in oriented polymers [13–16] and cholesteryl acetate [17]. The appearance of the long periods is also due to the alternation of less ordered amorphous regions with more ordered crystalline regions. The crystalline intensities sample a continuous molecular transform of the substituent molecules, whereas the amorphous scattering gives a spherically average continuous transform.

As such it is possible to evaluate the fractional composition of amorphous and crystalline regions. The order of the long period was estimated from the angular positions of the reflections by interpolating a smooth curve to separate the sharp reflection from diffuse scattering. The sharpness of the maximum may be due to the existence of domains in the unoriented solid crystal in which the long axes of the molecules are all pointed along a single axis. The long period was estimated to be 119.4 Å. The corrected period was obtained using the method of Tsvankin [18] was found to be 144 Å. The length of the crystalline part was determined to be nearly equal to that of the amorphous part, each being equal to 72 Å. It was verified that the amorphous regions did not show any appreciable dependence on the rate of cooling or surface effects. This was done by altering the conditions of preparation of the samples.

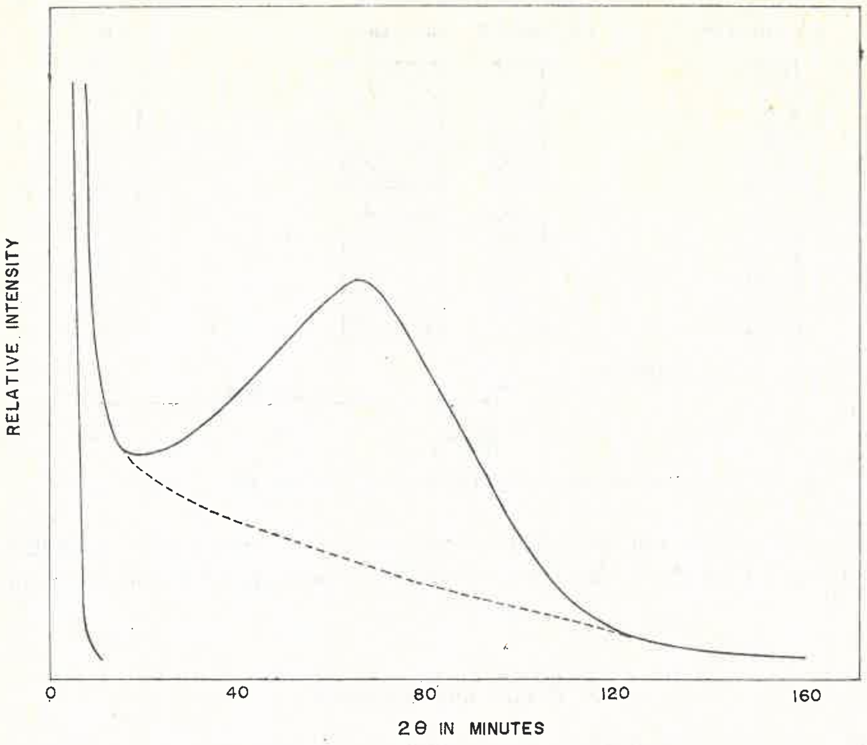

Fig. 3. Low angle scattering curve of cholesteryl ethyl carbonate

The results are almost identical to those obtained for cholesteryl methyl carbonate except for a slight change in the periodicity of the amorphous and crystalline regions which may be expected since the cholesteryl ethyl carbonate has an additional CH_2 group which increases the length of the molecule. This investigation establishes that the solid state consists of amorphous and crystalline regions, the number and size of which are approximately equal.

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