Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: D. Krishnegowda , S. R. Kumaraswamy , M. S. Madhava , R. Somashekar & D. Revannasiddaiah (1994): Optical Properties of Spherulites of Cholesteryl-do-decyl Carbonate, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 250:1, 21-30

To link to this article: http://dx.doi.org/10.1080/10587259408028189

Mol. Cryst. Liq. Cryst., 1994, Vol. 250, pp. 21–30
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Printed in the United States of America

Optical Properties of Spherulites of Cholesteryl-do-decyl Carbonate

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(Received September 10, 1992; in final form July 14, 1993)

We report here some very interesting optical textures exhibited by a pure cholesterogenic compound viz., Cholesteryl-do-decyl carbonate. It also exhibits ringed spherulitic texture when crystallized at different temperatures. The observed ring spacing is found to increase with the increase of crystallization temperature and we were also able to determine Avarami's constants by studying the growth rate of these spherulites. Light scattering and optical diffraction studies have been carried out using optical textures exhibited by the sample. The local order parameters corresponding to untwisted nematic structure in the cholesteric layer has been estimated at various temperatures in the cholesteric phase using the measured refractive index and density data.

Keywords: spherulites, optical diffraction, Avarami's constants, cholesteryl-do-decyl carbonate

INTRODUCTION

Cholesteric compounds are extensively used as one of the components of display materials. As such optical studies of cholesteric compounds are of great importance and numerous earlier investigations on optical textures, optical scattering, growth kinetics and various other physical properties have been carried out to obtain information about the molecular arrangement in the cholesteric phase.[1–8] In this paper we report optical studies and kinetics of spherulite growth in a pure cholesteric compound viz., cholesteryl-do-decyl carbonate (CDC) which have not been reported so far. We are also interested in looking at the effects of long chain methylene groups present in CDC molecule on various parameters.

EXPERIMENTAL

The cholesteryl sample used in this investigation was supplied by M/s Dynamic Research Application, Baroda, (India). Owing to the limited quantity of the sample that was available, no further purification of the sample was attempted. The solid-cholesteric and cholesteric-isotropic transition temperatures were determined using

the polarizing microscope in the heating mode, and are respectively 59° and 73°C. These values broadly agree with the reported values.[9] It is possible to grow ringed spherulites by quenching the sample to any desired temperature, referred as temperature of crystallization, even below solid-cholesteric transition temperature.

REFRACTIVE INDICES AND DENSITY

The refractive indices n_1 and n_2 in the cholesteric phase and n_l in the isotropic phase were measured for λ5893 Å, using Abbe refractometer, the techniques of measurements being the same as adopted earlier.[7] Here, n_1 and n_2 ($n_1 > n_2$) respectively correspond to the cases when the electric vector lying in the plane of the cholesteric layer and normal to it. The density measurements for the sample at different temperatures in the cholesteric and isotropic phases were carried out by the capillary tube method in the cooling mode. Measurements below 59°C were carried out in supercooled cholesteric phase. Figure 1 shows the variation of the refractive indices and density as a function of temperature. The measurements of the temperatures, refractive indices and densities are estimated to be correct to within ±0.2°C, 0.001 and 0.001 gm/cm^3, respectively.

OPTICAL TEXTURES

For the observation of the optical textures exhibited by CDC the specimens were prepared by melting a small quantity of sample between the microscope slide and cover glass at about 80°C and the molten sample was allowed to cool slowly on the stage of the polarizing microscope. When the specimen is allowed to cool slowly

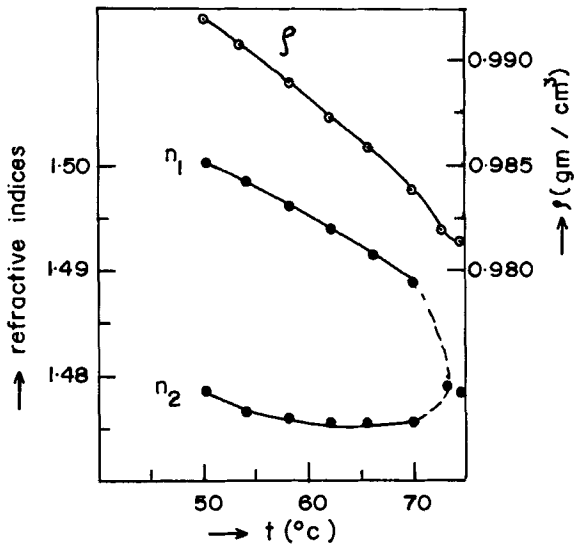

FIGURE 1 Variation of density and refractive indices with temperature.

from its isotropic melt, the birefringent droplets with crossed extinctions shown in Figure 2 are observed and they persist up to a temperature of about 50°C and then crystallize into the well-known spherulitic textures, see Figure 3(a, b). These spherulitic textures are metastable and in the course of an hour or two they transform into the textures of the form shown in Figure 3(c, d). Further, when this specimen is heated slowly to its cholesteric phase the textures shown above undergo transformation into a deformed spherulitic texture. The microstructure of the deformed spherulite was found to consist of small focal-conic domains symmetrically arranged

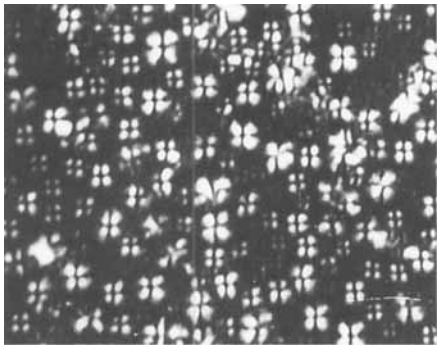

FIGURE 2 Microphotograph of birefringent droplets exhibited by cholesteryl-do-decyl carbonate. Crossed polarisers. 1800 X.

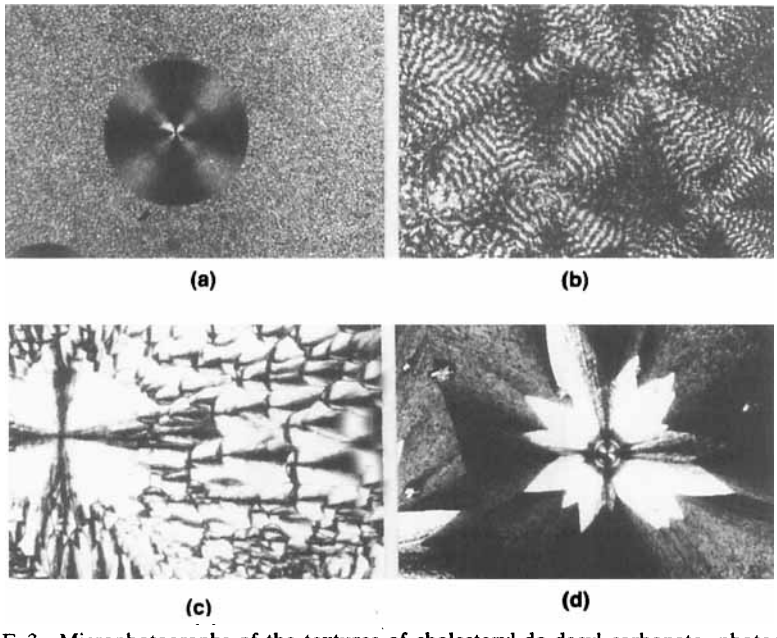

FIGURE 3 Microphotographs of the textures of cholesteryl-do-decyl carbonate, photographed between crossed polarisers. (a) A crystalline spherulite advancing into the cholesteric region, photographed at room temperature. 200 X. (b) A ringed spherulite texture grown at a temperature of 42°C. 250 X. (c and d) Textures obtained after transformation of the metastable texture in 3(a). 250 X.

within the spherulites. The photographs shown above have been obtained with the specimens between crossed polarizers, using a polarizing microscope. The thickness of the specimen was about 25 μm.

OPTICAL SCATTERING

The birefringent droplets shown in Figure 2 also exhibit the low angle H_v and V_v patterns. Figures 4(a) and 4(b) reproduce respectively the patterns recorded by us using the similar set up described earlier with He-Ne laser.[5] The patterns extend here over an angular diameter of about 4°. The typical cross and four-leaf clover patterns obtained with these indicate the radial-spherulite like molecular arrangement in cholesteric layer.

OPTICAL DIFFRACTION AND HELICAL PITCH

Figure 5 shows the low angle optical diffraction ring obtained with the ringed spherulites of CDC. As in the earlier cases[4,5] it is found that the diffracted light

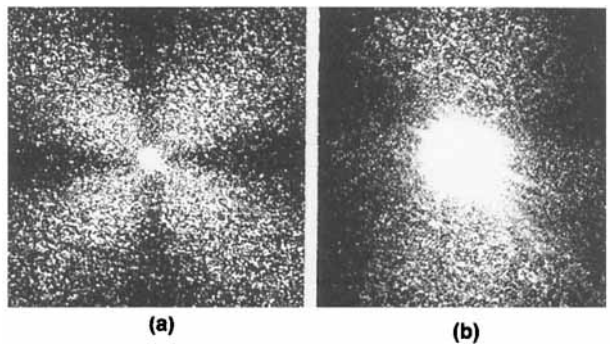

FIGURE 4 Low angle optical scattering patterns exhibited by the texture in Figure 2. (a) H_v and (b) V_v.

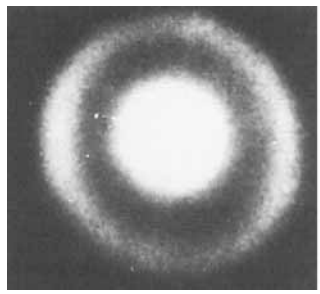

FIGURE 5 Diffraction pattern exhibited by the ringed spherulite texture shown in Figure 3(a), photographed with light of wavelength 5461 Å.

along any direction is polarized with its vibration direction transverse to the corresponding radius of the spherulite. The ring spacing d in the ringed spherulites which is equal to half the pitch distance ($d = p/2$) of the helicoidal arrangement may be calculated directly using a microscope with a micrometer eyepiece or from Bragg's equation $d = \lambda/\sin\theta$, where λ is the wavelength of the light used and θ is the angle of diffraction. The value of d is found to vary with the crystallization temperature of the specimen, i.e., the temperature at which the ringed spherulites are grown isothermally.[3] Figure 6 shows the variation in the measured values of the pitch p with respect to the crystallization temperature. It may be seen from this figure that the ring spacing d is smaller if the ringed spherulites are formed at lower temperatures of crystallization. At higher temperatures the rings become widely spaced. This increase in pitch can be attributed to the thermal expansion and also may be due to librational motion of the molecules about the helical axis. It may be mentioned here that the ring structure is hardly visible in the spherulite textures formed at room temperatures and below.

GROWTH KINETICS OF SPHERULITES

The radial growth of liquid crystalline and polymer spherulites depends primarily on the temperature of crystallization and surface geometry of the specimen. Microscopic, dilatometric and light depolarization methods are in use to determine the growth rates of such spherulites.[2,3,10] Here, we report some of the results of our investigation on the isothermal crystallization of spherulites of CDC using microscopic method.

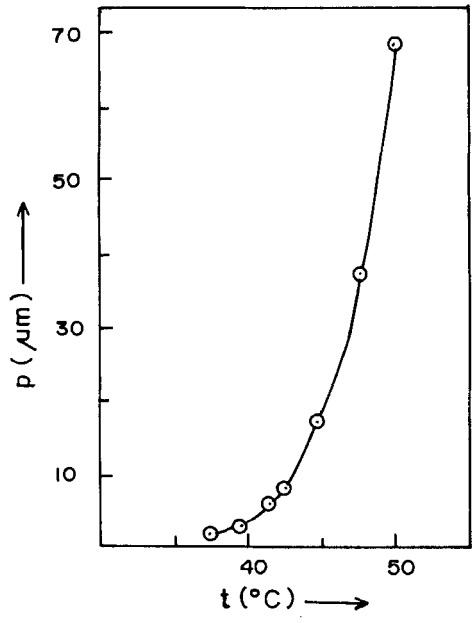

FIGURE 6 Variation of helical pitch P with crystallization temperature.

In order to investigate growth rates from the microscopic method, the specimen, taken between the slide and cover glass, was first heated to its molten state and cooled down to a required temperature below solid-cholesteric transition temperature, i.e., to a temperature at which the isothermal crystallization is to be tested. When the growth of spherulites begins to occur radially, at different centres of nucleation, the radii of the spherulites were measured as a function of time using a polarizing microscope with a micrometer eyepiece. The direct measurements were possible because we could get an isolated and radially symmetric spherulite in the field of view of the microscope. Further, the growth rate was also very small. Figure 7 shows the variation of spherulite radius R with time t' at various crystallization temperatures. It may be seen from the above figure that the radius of the spherulite is a linear function of time at any given crystallization temperature. It is also found from the measurements on different spherulites that all the spherulites at a given crystallization temperature grow at the same rate. The growth rates $G(=dR/dt')$ determined from the slopes of straight lines of Figure 7 are also shown graphically in Figure 8. The results shown in the above figures are similar to those reported by Adamski *et al.*[3] in the case of cholesteryl nonanoate. Studies on the growth kinetics of cholesteric spherulites of some cholesteryl esters[2,8] however

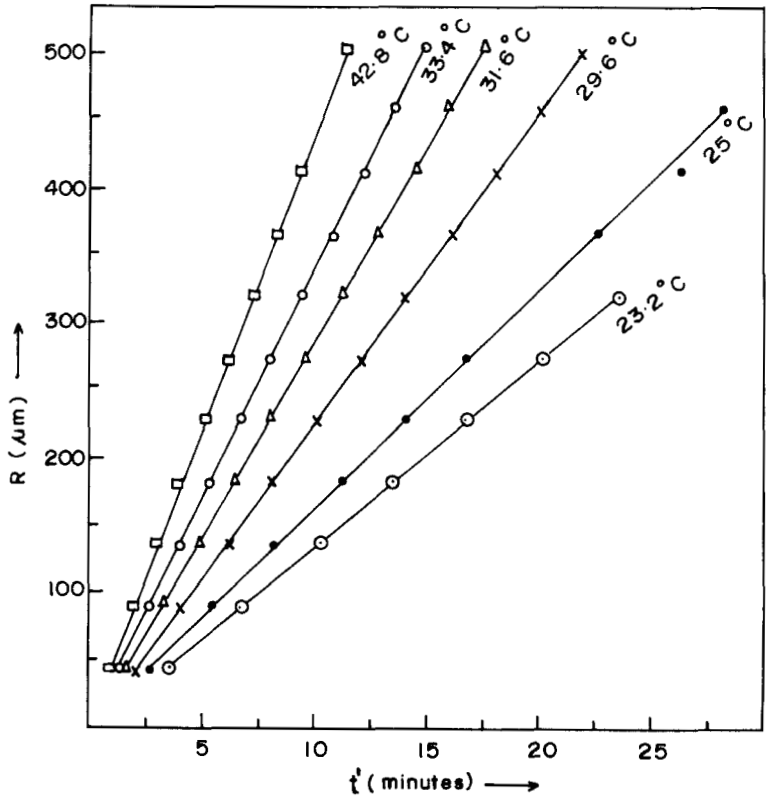

FIGURE 7 Variation of spherulite radius R with time t' at various crystallization temperatures.

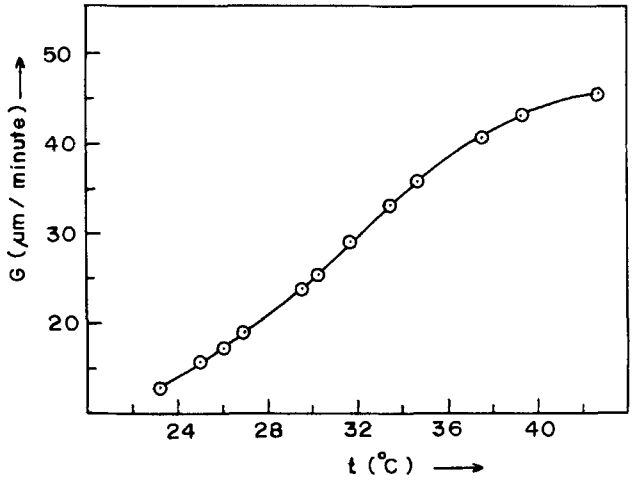

FIGURE 8 Variation of spherulite growth rate with temperature.

reveal that the growth rate of cholesteric spherulite radius is a decreasing function of temperature. This may be due to the fact that the growth rate in the mesophase is controlled by secondary nucleation process.

According to Jabarin and Stein[11] and Adamski *et al.*,[3] the growth rate of crystalline spherulites depends not only on the temperature of crystallization but also on the free energy ΔF and activation energy ΔE for the isothermal crystallization. The dependence of these quantities can be expressed by a simple relation $G = G_0 \exp[-(\Delta F + \Delta E)/kT]$, where G_0 is a constant. If the temperature of crystallization is lower than $T_{G(\max)}$, the temperature corresponding to the maximum value of G, we can neglect the influence of ΔF on the process of spherulite growth. Therefore, at all temperatures $T > T_{G(\max)}$, the growth rate varies as $G = G_0 \exp(-\Delta E/kT)$. The activation energy ΔE for the isothermal transformation is determined from the slope of the straight line graph of $\ln G$ versus $1/T$ and is found to be equal to 0.6 eV.

Adamski *et al.*,[3] have also described the isothermal crystallization process in the cholesteryl sample of constant volume but varied weight using the relation $(V - V_s)/V = \exp(-kt^n)$. Here, V is the volume of the specimen confined to the field of view of the microscope, after the crystallization process and V_s is the volume of the spherulite formed in volume V at time t'. Following the same procedure, we have estimated the well-known Avarami constants n and k in the case of CDC. The values of V_s at various crystallization temperatures and the volume V after crystallization process in each case were determined directly using a microscope. Table I gives the values of n and k obtained at various temperatures of crystallization. As may be seen from the Table I that the value of n is of the order 2 in all temperatures indicating that in the cholesteric-solid transformation the nuclei appear to be disks.[12] The number of disks increases with time and the disks elongate into rods as the transition proceeds. The parameter k in Table I is found to increase

TABLE I

The values of Avarami's constants n and k determined for Cholesteryl-do-decyl carbonate by the microscopic method

Temp (°C)	25	26	27	29.6	30.2	31.6	33.4	34.5	42.8
n	2.0	2.05	2.0	2.08	1.99	2.05	2.06	1.97	1.94
k(1/min^2)	2.49 x10^{-4}	2.49 x10^{-4}	3.35 x10^{-4}	3.53 x10^{-4}	5.53 x10^{-4}	6.11 x10^{-4}	8.25 x10^{-4}	9.58 x10^{-4}	1.602 x10^{-3}

roughly linearly with the temperature of crystallization and is in conformity with the results reported by Adamski *et al.*[3]

POLARIZABILITIES AND LOCAL ORDER PARAMETER

In order to calculate the polarizabilities and local order parameter corresponding to the untwisted nematic layer in the cholesteric phase the measured values of the refractive indices n_1 and n_2 are expressed[13] as $n_2 = n_0$ and $n_1 = (n_e + n_0)/2$, where n_e is parallel and n_0 is perpendicular to the local nematic director. Using the well-known Lorenz-Lorentz relation the mean polarizability $\bar{\alpha}$ in the isotropic phase is calculated from the index and density data for the liquid phase. In determining the effective polarizabilities α_e and α_0 at different temperatures in the cholesteric phase, earlier investigators have used Lorenz-Lorentz relation. We would like to emphasise that for substances showing low birefringence, it is immaterial whether one uses Lorenz-Lorentz, Vuks or Neugebauer relations to calculate the effective polarizabilities, since all of them would give consistent results. For the sake of completeness and since the density data are available, we have used Neugebauer relations to calculate α_e and α_0 at different temperatures in the cholesteric phase.

The local order parameter corresponding to the untwisted nematic layer in the cholesteric phase can be readily determined using the relation $S_{\text{loc}} = (\alpha_e - \alpha_0)/\Delta\alpha_m$, if the value of the anisotropy of molecular polarizabilities $\Delta\alpha_m$ is known. Since the density and the refractive indices are not measured in the crystalline phase, the following procedure was adopted in estimating the value of $\Delta\alpha_m$. The structure of the molecule under discussion is similar to that of cholesteryl esters of fatty acids, except for the fact that there are differences with regard to the number of methylene groups and two extra C—O bonds. Therefore it may be assumed that the contribution of the central rigid portion of the molecule to the optical anisotropy is the same in both the cases. Data on the polarizability anisotropy $\Delta\alpha_m$ of homologues of cholesteryl esters of fatty acids have been reported earlier.[13] Using these data and also knowing the additional contribution to the optical anisotropy due to methylene groups and the two C—O bonds from the values of bond polarizabilities, the value of $\Delta\alpha_m$ in the case of CDC was estimated

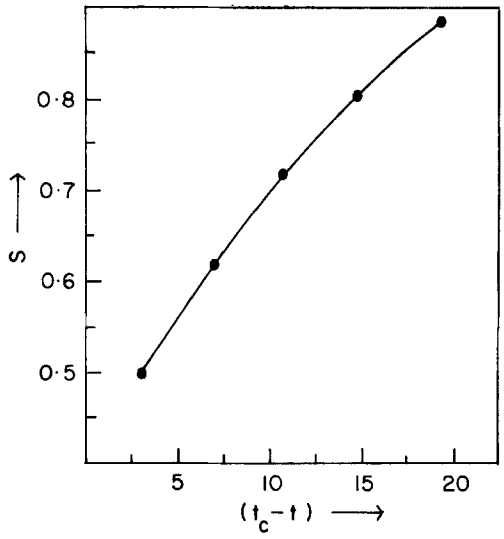

FIGURE 9 Variation of local order parameter S with $(t_c - t)$ in °C.

and found to be 8.61×10^{-24} cm^3. The local order parameter determined for this sample at different temperatures is shown graphically in Figure 9.

CONCLUSION

Optical and light scattering studies indicate that there is continuous and periodic variation of the refractive index of the spherulites for the light polarized transverse to the radial direction. This is in conformity with the earlier works of Stein *et al.*[1,2]

The periodicity of the ring structure in the crystalline spherulites changes with the temperature of crystallization.[14,15]

Growth kinetics of crystalline spherulites presented here show that in the cholesteric-solid transformation nuclei appear to be disks and the disks elongate into rods as the transition proceeds.

The observed variation of the local order parameter, corresponding to the untwisted nematic layer in the cholesteric phase, with temperature is consistent with the Maier-Saupe model of pure nematic compounds.

The above studies indicate that the long chain of methylene groups has insignificant effect on the observed parameters due to the fact that the cholesteryl group plays a dominant role.

Acknowledgment

One of us (S. R. K.) is thankful to the University of Mysore, Mysore, for the award of a University Post-Graduate Fellowship.

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