Light scattering study of the isotropic-to-blue phase transition in cholesteryl oleyl carbonate (COC) and its mixtures with a nematogen

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Light scattering experiments have been performed on cholesteryl oleyl carbonate (COC) and its mixtures with a nematogen in order to investigate pretransition phenomena accompanying the transition from the isotropic to the blue phase. Estimates of the critical temperature for the flat-spiral ($m = 2$) mode have been obtained in each case. The critical temperatures approach the transition temperature, T_c, in the mixtures, probably due to an impurity-induced blurring of the phase transition. Measurements of the optical rotatory power have also been carried out on pure COC as well as its mixtures with the nematogen and possible origins for the pretransition phenomena observed are discussed.

1. Introduction

The blue phase is a generic term for a family of optically isotropic, though liquid crystalline, phases that are stable over a small range of temperature just below the clearing point in spontaneously twisted mesophases of small pitch. The formation of blue phases is limited to systems with chiral symmetry. There is a critical pitch, however, above which these phases do not form and the value of this pitch depends sensitively on molecular interactions [1, 2]. Theoretical phase diagrams using the Landau-deGennes formalism have been used to predict blue phase sequences though experimental confirmation of the details appears incomplete.

The mechanism of the weakly first order transition from the isotropic (I) phase to the blue phase (BP) has generally been described using the Landau expansion of the free energy density in powers of the order parameter [3, 4]. This expansion is strictly valid only for cholesteric (Ch) liquid crystals and its extension to BPs assumes that the coefficients are very similar in the cholesteric and blue phases. Since the (chiral) ordered phase has a traceless, tensorial order parameter with five independent components, it can be described by five normal modes. Using the notation of Shtrikman and coworkers [5], $m = \pm 2$ represents a flat spiral mode; $m = \pm 1$, a conical spiral mode, and $m = 0$, a nematic-like mode. The modes associated with negative m have opposite handedness from their positive-m counterparts. The amplitudes of these modes diverge at critical temperatures T_m^* where m is the mode label. Each critical temperature may be regarded as the temperature at which the mode would reflect a second-order transition in the system if the experimentally observed (weakly first-order) transition did not intervene at T_c. Clearly a helically ordered mesophase is more complicated than a nematic whose behaviour may be described by a single mode.

There are a few reports of experimental work on the I → BP phase transition. Early studies [6–8] of the transition used photon correlation spectroscopy because of its ability to follow the temporal evolution of macroscopic fluctuations in the sample. The time window on the order of 10^{-3} to 10^{-7} seconds that this technique offers is ideally suited to a study of pretransitional dynamics. Keyes and his associates [6] were the first to explicitly recognize the existence of a BP in their light scattering study of the transition to the ordered fluid phase in cholesteryl oleyl carbonate (COC). Their report of a single exponential correlation function in the pretransition region was later amended to include the presence of a second exponential with a correlation time differing from the first by a factor of 5 [7]. Keyes and coworkers [7] found that correlation times and a viscosity coefficient had a non-linear temperature dependence in this domain and suggested that complex correlation functions close to the transition were unique to BP-forming cholestogens. These results differ from those of Harada and Crooker [8] who found a linear temperature dependence of absolute intensity and linewidth and a continuous change in light scattering properties at the phase transition in an earlier study of COC.

Recent studies [9–11] of the I → BP transition have used optical rotation measurements that, in the absence of mode coupling, reflect the behavior of the $m = 1$ mode alone [4, 5]. The variation of optical activity with temperature in cholesteryl esters has been measured by Atkinson and Collings [9] who have found that it is generally in accord with theoretical models except near the transition. They ascribe the discrepancy to the formation of a biphase in a narrow temperature region in contrast to Demikhov and Dolganov [10] who attributed it to coupling between $m = 2$ and $m = 1$ modes. Atkinson and Collings [9] also find that the shift in $T_1^* - T_c$ with chirality is contrary to theoretical predictions. The authors ascribe this feature to differences between the Ch and blue phases that have not been recognized in the theoretical models. Working with a different system of higher chirality, however, Collings and his associates [11] later demonstrated that their results agreed with theoretical predictions even close to the transition. The reason for the different behaviour displayed by the two systems remains unclear.

In the light of the divergent results of Harada and Crooker [8] and Mahler *et al.* [6], we felt that it was appropriate to reconsider the light scattering and optical rotatory properties of COC, especially in the transition region. Estimates of T_2^* have been obtained in COC and its mixtures with a nematic [N] liquid crystal, methoxy-benzylidene-p,n-butylaniline (MBBA), in order to investigate the dependence of the critical temperatures on changes in chirality induced by admixture with a nematogen. We were able to obtain a value for T_1^*, however, only in the case of pure COC. In the absence of a phase diagram for the MBBA/COC system we have qualitatively examined the behaviour of different modes only in the pretransition region. The optical rotation component of the present study supplements earlier data obtained with mixtures of cholesterol esters in highlighting the role of molecular interactions that may well be different in mixtures and pure compounds.

2. Experimental section

(i) *Sample preparation.* COC and MBBA were obtained from Aldrich Chemical Company and Eastman Kodak, respectively. Samples were filtered through $0.1\,\mu$ or $0.5\,\mu$ filters with the finer filter being used with the less viscous MBBA mixtures. In the light scattering studies, the samples were then loaded into cylindrical glass cells which

had a pair of diametrically opposed flat windows to minimize internal reflections of the laser beam. Compositions of mixtures stated below refer to mole percent (MBBA : COC).

(ii) *Photon correlation measurements:* Samples were mounted in a cell holder whose temperature could be stabilized to within ± 50 mK using a Lauda-Brinkman constant temperature circulator. A Malvern K7022, 64-channel real-time multibit correlator was used to record homodyne correlation functions which were then transferred online to a computer where further data analysis was carried out. The spectrometer was calibrated with an aqueous solution of polystyrene beads. A 14 mW Spectra-Physics He-Ne laser operating at 6328 Å with its plane of polarization perpendicular to the scattering plane was used as the light source. All spectra were recorded at a scattering angle of 90°. A sheet polarizer with an extinction coefficient of 10^{-4} for white light was used as an analyser.

(iii) *Data analysis.* Heterodyne correlation functions, $g(t)$, were obtained from the observed homodyne correlation functions assuming that the scattered light had a gaussian distribution [12]. Further analyses were performed on the heterodyne correlation functions so obtained.

Curve fits to the measured correlation functions using a multiexponential model equation:

$$g(t) \ = \ \sum_{i=1}^{n} a_i \exp\left(-t/\tau_i\right) \tag{1}$$

were carried out using a non-linear least-squares fit program based on the Marquardt [13] algorithm. The Durbin–Watson parameter [14] that measures the average serial correlation between residuals was used as a goodness-of-fit criterion. The number of terms, n, in the model equation was chosen so that (a) addition of further terms did not increase the Durbin–Watson parameter, and (b) the root-mean-square deviation decreased by less than half consequent to such an addition.

(iv) *Optical rotatory power.* The optical rotatory power of the samples was measured using a Perkin-Elmer Model 120 spectropolarimeter with the 5890 Å line from a sodium lamp. The cells were flat-walled cuvettes with a pathlength of 2 mm. Temperature control to ± 50 mK was achieved with a constant temperature circulator.

3. Results and discussion

The Landau expansion to fourth order contains four quadratic terms with the coefficients a, b, c, and d. The coefficients for the third and fourth terms are μ and λ, respectively. The temperature dependence of a is described by $a = a_0(T - T^*)$ where T^* is the second order transition temperature for a racemic mixture. To second order, the Landau expansion of the free energy can be written as [5]

$$F - F_0 \ = \ \frac{1}{2}\sum_{m} \int d^3q \left[a - mdq + \left\{ b + \frac{c}{6}(4 - m^2) \right\} q^2 \right] |\varepsilon_m(q)|^2, \tag{2}$$

where m is the label for the mode, $\varepsilon_m(q)$ is its amplitude and $\vec{q}$ is the wave vector. It turns out that each of these modes diverges at a critical temperature T_m^* given by the following relations where q_0 denotes the chirality of a system with pitch, P, $q_0 = 4\pi/P = d/b$:

$$T_{\pm 2}^* \ = \ T^* + bq_0^2/a_0, \tag{3}$$

$$T^*_{\pm 1} = T^* \pm 1/(4(1 + c/2b))bq_0^2/a_0, \tag{4}$$

$$T^*_0 = T^*. \tag{5}$$

With the assumption that the modes are uncoupled, Hornreich and Shtrikman [3] have shown that measurements of the light scattering intensity at non-zero scattering angles reflects the contribution of the $m = \pm 2$ mode alone. This finding is supported by optical studies of a BP system in which the contributions of the other modes were indeed found to be negligible [15]. We have accordingly used the light scattering intensities to arrive at a value for T^*_2. In the same limit of uncoupled modes, Shtrikman and coworkers [5] have also shown that temperature dependent measurements of optical activity yield a value for T^*_1. Furthermore, the experimentally observed $I \to$ BP transition temperature, T_c, is greater than the T^*_m, with $T_c > T^*_2 > T^*_1$. Comparing the free energies of the I and Ch phases, T_c can be related to T^*_m in terms of the Landau expansion to fourth order. If it is assumed that the Ch and blue phases are thermodynamically very similar (at least with respect to the I phase) the difference between T_c and the critical temperatures of relevance to us is given by [5, 9]:

$$T_c - T^* = \mu^2/27\lambda a_0 + (3/4)bq_0^2/a_0, \tag{6}$$

$$T_c - T^*_2 = \mu^2/27\lambda a_0 - (1/4)bq_0^2/a_0, \tag{7}$$

$$T_c - T^*_1 = \mu^2/27\lambda a_0 + \frac{1}{4}\left[\frac{2 + 3c/2b}{1 + c/2b}\right]bq_0^2/a_0. \tag{8}$$

It is evident that with increasing chirality, T_c tends to T^*_2 but diverges from T^*_1 (other coefficients in the free energy expansion remaining constant). There is evidence, however, that close to the transition the assumption of independent modes breaks down [11]. We shall discuss this point further in a later section.

We have not identified the BP(s) present in the MBBA/COC system but assume that the BP common to all of the compositions studied here is BPI. We make this assumption in view of the demonstrated stability of BPI (vis-a-vis BPII and BPIII) at larger pitches.

3.1. Light scattering

(i) *Scattering intensity.* Integrated intensity measurements were performed on COC and MBBA/COC mixtures in the polarized (VV) and depolarized (VH) configurations. Since multiple runs were made on the each sample as well as on different batches of the same composition, only representative plots of the inverse of these intensities are presented as a function of temperature in figures 1 to 3 for COC and MBBA/COC (50 : 50 and 67 : 33 mole per cent) solutions. The experimental conditions were modified for COC to compensate for the weak scattering in the isotropic phase so that isothermal values of the scattering intensity cannot be compared among the three samples.

The inverse polarized scattering intensity is related to temperature by $I_{VV}^{-1} \alpha$ $\mathbf{a}(T - T^*_2)$ where T^*_2 is the critical temperature for the $m = 2$ mode. The values of T_c, T^*_2, and $\mathbf{a}$ obtained in this manner are compiled in the table. Different runs on the same sample or on different batches of the same composition resulted in temperature variations of less than a degree, without change in the behaviour observed. The $I \to$ BP transition temperature, T_c, was identified as the temperature at which the inverse of
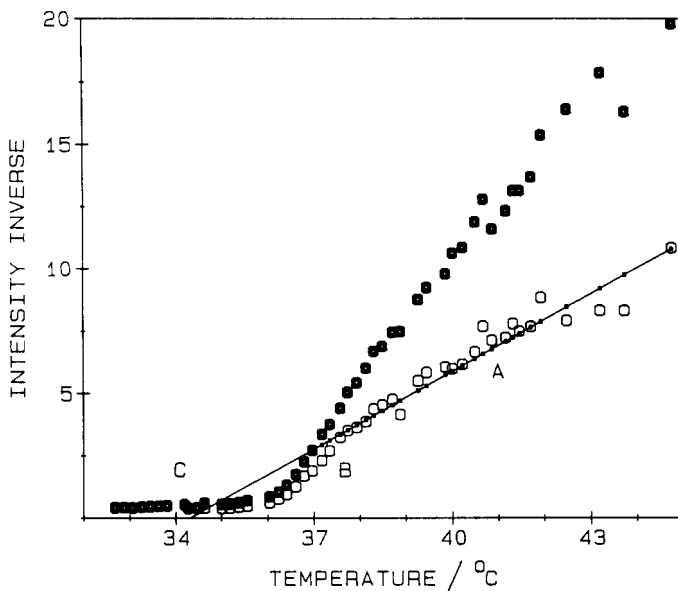
Figure 1. A plot of the inverse of the scattering intensity (in arbitrary units) as a function of temperature for COC. Filled symbols: depolarized scattering; open symbols: polarized scattering. The line represents a linear least squares fit to $(T - T_2^*)$.

Figure 2. A plot of the inverse of the scattering intensity for MBBA : COC : : 50 : 50. (See caption to figure 1 for details.)

the intensity either levelled off or approached zero. We emphasize that while the values of T_c and T_2^* varied from run to run in the manner described above, the difference between these quantities remained relatively constant. To check the T_c values obtained in the light scattering experiment, the samples were also visually examined as a function of temperature in the same 10 mm pathlength cell in reflected
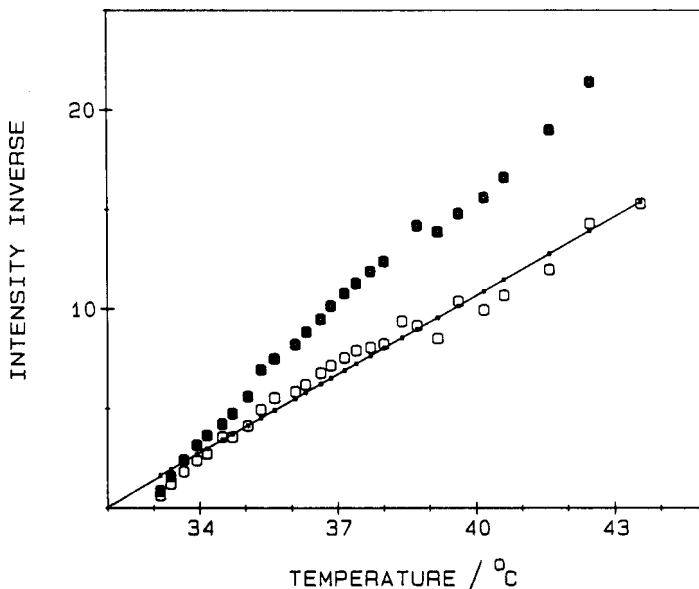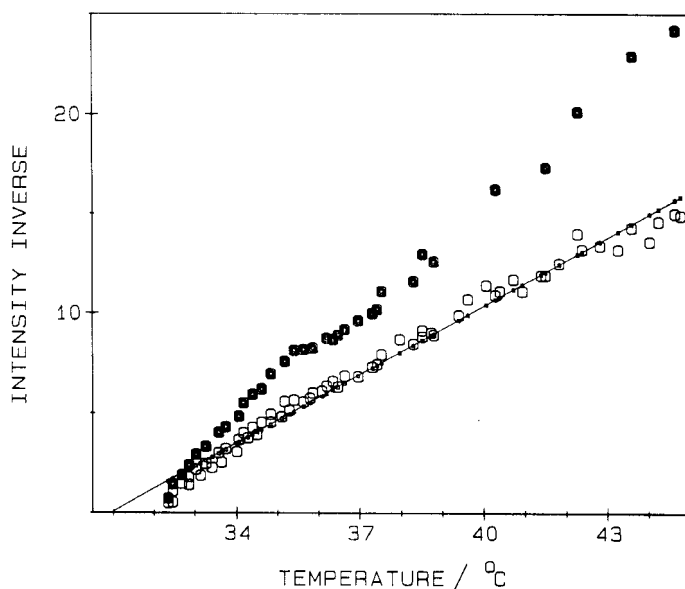
Figure 3. A plot of the inverse of the scattering intensity for MBBA:COC::63:37. (See caption to figure 1 for details.)

Parameters of the MBBA/COC mixtures (all temperatures in °C).

Sample (MBBA : COC mole %)	0 : 100	50 : 50	63 : 37
T_c (visual: 1 cm pathlength cell)	36·0	—	32·5
T_c (light scattering)(T_c^{ls})	36·4 ± 0·3	33·8 ± 0·5	32·4 ± 0·1
$(dI_{VH}^{-1}/dT)/(dI_{VV}^{-1}/dT)$	2·1	1·5	1·5
a (arbitrary units)	1·0 ± 0·1	1·3 ± 0·3	1·1
$J^e/k_B T$ (°C^{-1})	0·04	0·017	0·015
T_c (optical rotation)	35·8	33·8 ± 0·7	34·0
T_c (visual: 0·1 cm pathlength cell)	35·4 ± 0·4	33·0 ± 0·3	33·9 ± 0·1
T_2^*	34·0 ± 0·3	32·6 ± 0·7	31·0 ± 0·2
$T_c^{ls} - T_2^*$	2·4	1·2	1·4
T_1^*	32·0 ± 0·5	—	—

light; the $I \rightarrow$ BP transition was identified with an obvious change in the colour of the sample and the temperatures so obtained were within 0·2° of those measured in the light scattering study. Increasing turbidity was noted in all of the samples starting about 0·8° above the observed T_c, possibly due to the increasing correlation length of the fluctuations.

Three regions are discernible in the I^{-1} versus temperature plot (figure 1) for pure COC: the isotropic phase is denoted by A, while the pretransition region and the BP (where I^{-1} levels off) are represented by B and C respectively. At the lowest temperatures of this study, it is quite possible that the BP zone also contains the Ch phase. The flattened portion of the curve (region C) is not evident with the mixtures and we attribute this to destabilization of the BP with increasing MBBA. Around the transition, the samples with increasing MBBA reflected light in the blue-green region of the spectrum, while COC was violet in color in reflected light; this indicates that the pitch increases with increasing MBBA content for the compositions examined here. An

increase in pitch would destabilize the BP. The ratio of the slopes in region A of the plots of I_{VH}^{-1} to I_{VV}^{-1} versus temperature (at $T \gg T_c$) is about 2 for COC and 1·5 for the samples with MBBA.

The values for $T_c - T_2^*$, at first glance, are surprisingly large for COC when compared to the values reported by Mahler *et al.* [6] as well as by Harada and Crooker [8] though the agreement between our estimate of T_c and that of Mahler *et al.* is quite good. Both of these groups report only a single critical temperature that they denote by T^* which we believe is comparable to our T_2^* inasmuch as the two were obtained through similar experiments. Harada and Crooker [8] have observed a much lower transition temperature and it is not clear that the transition, in their case, is indeed to the blue phase. The discrepancy between the results of Mahler *et al.* and our own thus lies with the measurement of T_2^*. It appears that Mahler *et al.* have obtained the critical temperature by extrapolating the I^{-1} data in the pretransition region (denoted by B in figure 1) rather than those in the isotropic phase, region A. We can obtain a value for T_2^* that is very close to their value using the former procedure, but this may be incorrect since it involves an application of the Landau-deGennes model close to the transition where mean-field theories are known to be inadequate.

Table 1 reveals that T_c tends toward T_2^* as half the COC in the sample is replaced with MBBA; there may be a weak increase as the MBBA content rises further, but this increase is within the bounds of experimental error. At any event, the decrease of $T_c - T_2^*$ with diminishing chirality that we have observed runs counter to the prescription of equation (7). Earlier workers have reported similar findings and we shall discuss this feature presently.

The ratio of the temperature dependence of I_{VH}^{-1} to I_{VV}^{-1} in COC (c. 2·0) is higher than that reported by Harada and Crooker [8] (1·448); once again, this discrepancy disappears if the ratio is measured closer to the transition. The value for the MBBA/COC solutions is quite similar to the value reported in COC by Harada and Crooker [8]. These workers have noted the discrepancy between their measurements and the prediction of a ratio of 1·3 by the Landau-deGennes model. We obtain a still larger ratio well into the isotropic phase.

(ii) *Depolarization ratio.* From the integrated polarized and depolarized intensity data we have calculated the depolarization ratio, ϱ, ($\varrho = I_{\text{VH}}/I_{\text{VV}}$) and have plotted this parameter as a function of temperature in figure 4 for the three samples of this study. Following Courtens [16], Schindler and Crooker [17] have suggested that the temperature variation of ϱ can be accounted for by:

$$\varrho = \varrho_0[1 - \tfrac{3}{4}(J^\varrho/k_B T)(T - T^*)], \qquad (9)$$

where k_B is the Boltzmann constant, $J^\varrho/k_B T$ represents the contribution of density fluctuations, and $\varrho_0 = 0·75$. Our fit to equation (9) is also shown in figure 4 where we have again set $T^* \equiv T_2^*$. Courtens [16] has pointed out that $J^\varrho/k_B T$ strictly includes the effect of particular impurities which scramble polarization; we shall assume that this factor affects each of our samples to the same extent. The values of $J^\varrho/k_B T$ for the three samples have been listed in table 1. It is clear that the limiting value of the depolarization ratio is close to 0·75 as expected from equation (9). We attribute the difference of about 3 per cent to the relative insensitivity of our apparatus to small changes in the depolarization ratio. Our value of $J^\varrho/k_B T$ is higher than that of Schindler and Crooker [17] ($0·025 \pm 0·002°C^{-1}$), possibly due to the larger temperature range spanned by the present study.
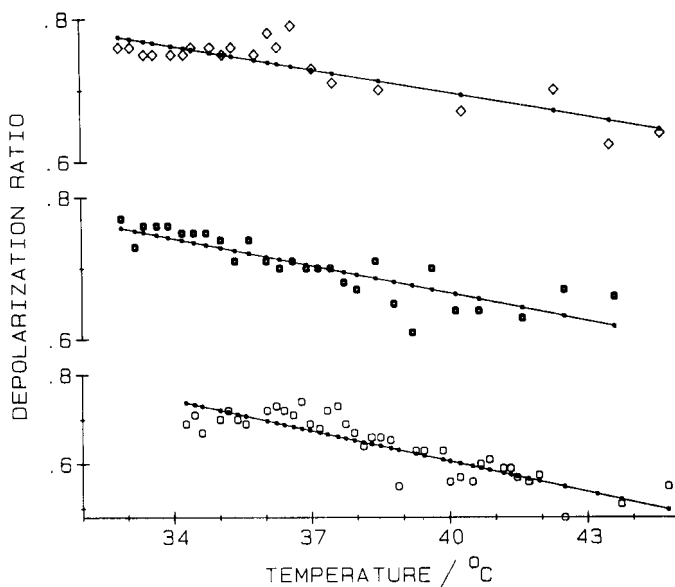
Figure 4.   Plots of the depolarization ratio versus temperature for COC (circles), MBBA:
   COC::50:50 (filled circles), MBBA:COC::63:37 (diamonds). The lines represent a fit
   to equation 9.

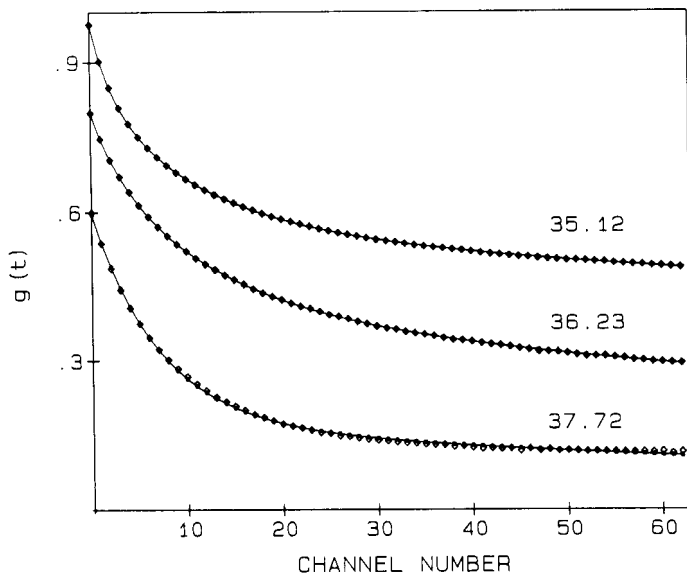Figure 5.   Typical correlation functions obtained at the temperatures shown (in °C) for COC.
   The lines are fits to multiexponential functions as discussed in the text. Each curve has
   been offset by an increment of 0·2 along the ordinate with respect to the one below for
   clarity.

(iii) *Correlation functions.* Typical correlation functions obtained in the polarized
(VV) mode are displayed in figure 5 for pure COC. Correlation functions of the
depolarized mode (VH) were qualitatively similar. The correlation functions could be
recorded with confidence only at temperatures $\leqslant T_c + 1\cdot5°$ since the intensity of the

scattered light was much too feeble at higher temperatures. Subject to the curve fitting criteria discussed above, it was found that the correlation functions could be fit by two exponentials for pure COC well into the isotropic phase ($T > T_c + 0.8°$). At lower temperatures, three exponentials were required for a fit of similar quality. The three exponential function was thereafter used at all lower temperatures, through the transition and into the BP. In the BP domain the correlation function grew weaker and a three exponential fit proved to be inadequate as well, possibly due to multiple scattering. Plots of the shorter correlation times (τ_1 and τ_2) are shown as a function of temperature in figure 6. (The variation with respect to temperature of the longest correlation time was similar and has not been presented.)
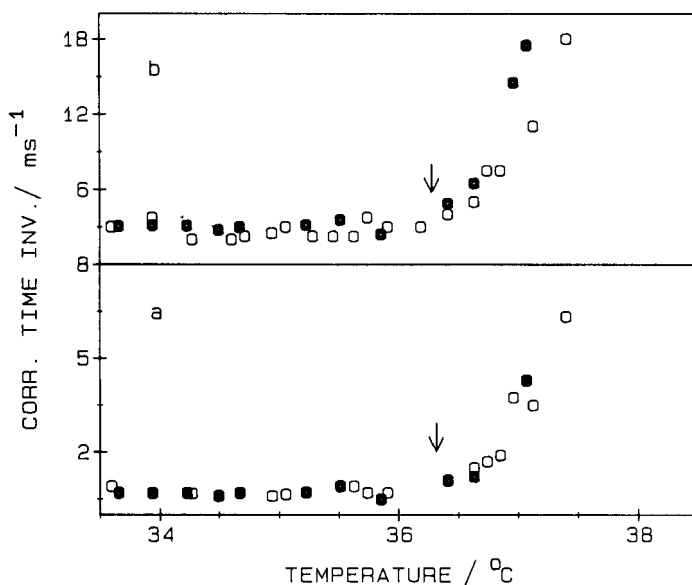
Figure 6. Plots of the inverse correlation times against temperature for COC $a : \tau_2^{-1}$; $b : \tau_1^{-1}$. The arrows indicate points of inflection.

A single exponential sufficed to describe the correlation function for the mixtures at $T > T_c + 1°$ for the 50 : 50 sample and $T > T_c + 0.4°$ for the sample with more MBBA. However, due to the weak scattering (especially at long times) at these temperatures, the entire correlation function of the mixtures could not be analysed. Plots of the correlation times so obtained are displayed as a function of temperature in figures 7 and 8. At lower temperatures, two exponentials were adequate to fit the recorded correlation functions of both samples, but we shall not discuss the behaviour of the additional exponential in view of the restricted temperature range over which it could be observed.

The temperature of onset of the additional exponential in the correlation function is similar to the temperature at which the sample was visually observed to increase in turbidity and is thus another manifestation of the pretransition. The values of τ_1 and τ_2 that we have measured in COC range from 50–400 μs and 150–1200 μs, respectively. It should be noted that Mahler *et al.* [6] report correlation times between 25 μs and 1000 μs while those measured by Harada and Crooker [8] lie between 12 μs and 2000 μs. The values of the shorter correlation times in the mixtures lie between 5–20 μs
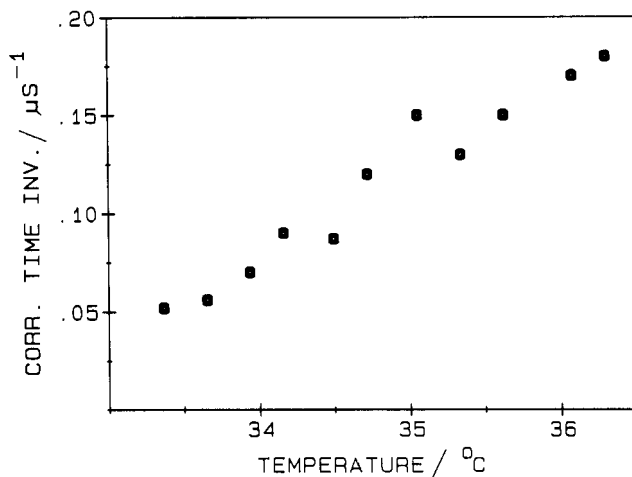
Figure 7. A plot of the inverse correlation time against temperature for the MBBA:
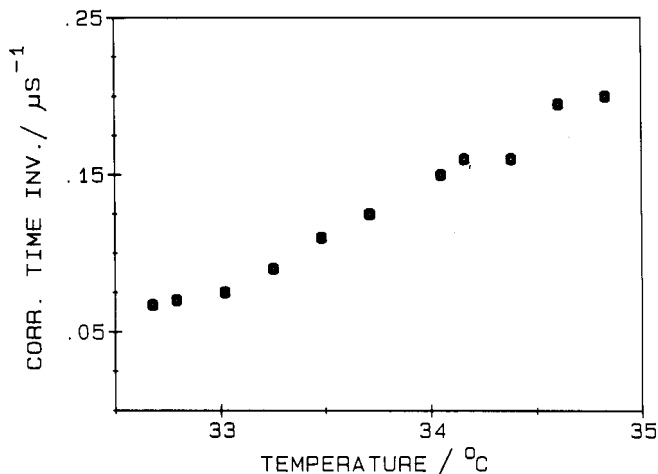COC :: 50 : 50 composition.

Figure 8. The temperature dependence of the inverse correlation time for the MBBA:
COC :: 63 : 37 composition.

and 5–15 μs for the 50 : 50 and 63 : 37 samples, respectively. We have presented all of the data obtained but shall henceforth confine our discussion to temperatures in excess of T_c since light scattering by the BP has added complexities.

An examination of figure 6 reveals that the correlation times of COC are markedly temperature sensitive at higher temperatures, whereas at lower temperatures they are essentially constant. The temperature of inflection (indicated by an arrow) separating these regimes is not very different from the value of T_c that was deduced from the scattered intensity plot (table 1). We therefore conclude that the levelling off of the correlation times as a function of temperature is also a manifestation of the $I \rightarrow$ BP transition and reflects stabilization of the mesophase against fluctuations of the order parameter. In figures 7 and 8 for the binary mixtures, however, the inflection temperature is much more indistinct.

The only model discussed in the literature that attempts to explain the origin of multiexponential correlation functions at temperatures higher than T_c is that due to Keyes and Yang [7]. These workers point out that in the general case where gradient terms are retained in the expansion and the order parameter is expanded to include a biaxial component, three lorentzians (exponentials) may be expected to contribute to the light scattering spectrum (correlation function) in the pretransition region of a cholestogen. The linewidths of these lorentzians are given by:

$$\left. \begin{array}{rcl} \Gamma_1 & = & \Gamma(1 + \xi_1^2 q'^2 + \tfrac{2}{3}\xi_2^2 q'^2) \\[4pt] \Gamma_{2A} & = & \Gamma(1 + \xi_1^2 q'^2 + 2\xi_1^2 q' q_0) \\[4pt] \Gamma_{2B} & = & \Gamma(1 + \xi_1^2 q'^2 - 2\xi_1^2 q' q_0) \end{array} \right\} \tag{10}$$

where Γ is the line-width at $T \gg T_c$, ξ_1 and ξ_2 are correlation lengths, and q' is the scattering vector. For a nematic, the last two exponentials collapse into one ($\Gamma_{2A} = \Gamma_{2B}$) since q_0 is zero. In the case of COC, the pitch is about $0.7\,\mu$ around the transition; for $90°$ scattering, this implies that $q' \sim 2q_0$. In this case equations (10) simplify to $\Gamma_{2A} = \Gamma(1 + 2\xi_1^2 q'^2)$, $\Gamma_{2B} = \Gamma$ and $\Gamma_{2A} > \Gamma_{2B}$. Γ_{2B} corresponds to the longest correlation time, since $\tau^{-1} = \Gamma$. We tentatively associate Γ_{2A} with the intermediate correlation time, τ_2, and τ_3 with Γ_{2B}. With these assignments, we find that $\xi_1 q_0$ is about 0.7 at $T_c + 0.2°$, a value close to that quoted by Keyes and Yang [12] for another cholestogen around $0.2°$ above its clearing temperature. A similar value is obtained if τ_2 and τ_3 are associated with Γ_{2B} and Γ_{2A}, respectively.

The single exponential function observed at high temperatures in the MBBA/COC solutions could be due to inadequate experimental resolution that militates against a distinction between Γ_{1A} and Γ_{2A} (or Γ_{2B}) if the two correlation lengths are similar. Nevertheless, it must be pointed out that if the two correlation lengths are similar for COC as well ($\xi_1 = \xi_2 = \xi$) and $\xi q_0 = 0.8$, then $\Gamma_1 \sim 5.2\Gamma$, $\Gamma_{2A} \sim 6.1\Gamma$ and $\Gamma_{2B} \sim \Gamma$. We have found, however, that $\tau_{n+1} > \tau_n$ by a factor of ~ 4 ($n = 2, 1$) for this compound. We conclude that the Keyes–Yang model is unable to explain the complete light scattering spectrum of COC though it is more successful in the solutions that are of lower chirality.

3.2. *Optical rotation*

Values of the optical rotation as a function of temperature are plotted in figure 9. The data for all of the samples indicates that the isotropic phase and the Ch phase are both levorotatory while the BP phase is dextrorotatory. The chiral phases are characterized by large values of the optical rotation, due to the so-called 'form' optical rotatory power. The $I \to$ BP transition has been taken to be the temperature at which the largest negative reading was noted, prior to the rise towards positive values. The samples were also visually examined in the same (1 mm) pathlength cell to check the transition temperature obtained in the optical rotation experiment. We felt that this would enable us to isolate cell geometry effects upon the transition in case the transition temperatures were found to be different from those obtained in the light scattering experiment. The T_cs estimated visually were within $0.8°$ of those measured in the optical rotation and light scattering experiment except for the sample with the highest MBBA content: in this case the transition occurred about $1.5°$ higher in the thinner cells. The reasons for this are not clear to us. In the MBBA/COC solutions
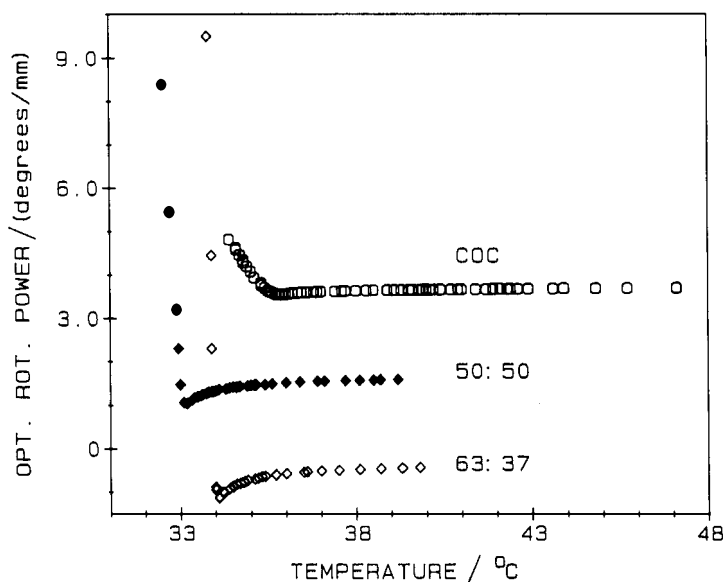
Figure 9. Representative plots of the temperature dependence of the optical rotatory power at 5890 Å for the compositions shown. Each curve has been offset by a factor of 2·0 along the ordinate with respect to the one below in the interest of clarity.

we again noticed shifts of the temperature scale with different batches/runs though the behaviour displayed was otherwise the same. At temperatures above the transition we could not visually detect an increase in sample turbidity due to the short pathlength of the cells. The transmitted light beam in the spectropolarimeter was also observed to be of unvarying intensity in this temperature range.

Using the Landau–deGennes framework, Shtrikman and coworkers [5] have pointed out that the values of the optical rotatory power is related to the temperature by:

$$\psi = \frac{k_{B}q'^{2}q_{0}}{48\pi\bar{\varepsilon}(a_{0}b)^{1/2}}\left[1 + \frac{c}{2b}\right]^{-3/2}\frac{T}{(T - T_{1}^{*})^{1/2}} + \phi_{0} \qquad (11)$$

where $\bar{\varepsilon}$ is the average dielectric constant and ϕ_{0} is the molecular optical rotatory power. We fit data obtained in the case of pure COC to equation (11) with ϕ_{0} equal to 2·7°/cm. We found that T_{1}^{*} (35·2°C) was close to T_{c} ($T_{c} - T_{1}^{*} < 0·5°$), typical of the values that Collings and his associates [9, 11] found in their study of other cholesteryl esters. Attempts to analyse the data obtained with the mixtures in this fashion were severely hampered by uncertainty in ϕ_{0} and the non-monotonic variation of ϕ close to T_{c} so that we were unable to arrive at confident estimates of T_{1}^{*} in these samples. It is noteworthy that $T_{2}^{*} < T_{1}^{*}$ for COC contrary to the prescription of equations (7) and (8).

Yet another interesting aspect of the optical rotation results is the increase of ϕ_{0} towards more negative values, forming a cusp in a narrow (ca 0·5°C) temperature above T_{c}. Atkinson and Collings [9] had attributed the phenomenon in neat cholesteryl esters to the formation of a biphase, but in a later study on mixtures of higher chirality [11] these authors accepted the mode coupling hypothesis proposed by Filev [18]. In terms of this model, the coupling introduces a contribution to ϕ of

opposite sign from that of the $m = 1$ mode; the strength of the coupling between the two modes (i.e., the non-monotonic component) is predicted to be larger as T_c approaches T_2^* as is indeed the case with our mixtures (vis-a-vis COC). Scrutiny of figure 9 reveals that the cusp is more pronounced in the case of the mixtures than it is for COC so that mode coupling may well be responsible for this feature. From a physical standpoint, we surmise that this feature reflects the amplitude of deviation from mean field behaviour when the I and blue phases are of opposed chirality. Should mode coupling close to the transition be important in our MBBA/COC mixtures, it may seem that the critical temperatures obtained in the light scattering study cannot be unambiguously identified with T_2^*. However, since the value for T_2^* was obtained by extrapolating the data in the isotropic phase rather than that in the pretransition region, we feel that our analysis is valid. Certainly, the effect of mode coupling upon the pretransition merits further exploration.

The results discussed above indicate a qualitative discord between theoretical predictions and the light scattering spectra. The light scattering correlation function becomes more complex at temperatures corresponding to the pretransition region and lower; we have limited ourselves strictly to a discussion of the data obtained above the phase transition but find that the only model addressing the origin of multimode decay cannot account completely for our results. The correspondence between theory and optical rotation data is apparently better, although we are limited to a qualitative consideration. The variation of T_2^* with chirality in our study appears to be supported by other reports in the literature even though it is at variance with theoretical predictions. We believe that an explanation of these features lies in the blurring effect that the addition of an 'impurity' has upon the phase transition of the parent compound. Thus, the addition of an impurity, in this case, MBBA, to COC should smooth the $I \rightarrow$ BP transition in the latter: the ordinarily first order transition might then be expected to take on an increasingly continuous aspect as reflected in the temperature dependence of scattered light intensity (figures 1–3) and correlation times (figures 7 and 8). More rigorously, MBBA may be regarded as ordering the isotropic phase by reducing the orientational mobility of COC, while inhibiting the ability of COC to order in the BP by virtue of its dissimilar molecular profile. This would result in a reduction in the order parameter discontinuity at the transition. One would also expect the actual transition temperature to approach the critical temperature as the impurity level rises and the data in table 1 bear this out. Indeed, it is possible that the decrease in $T_2^* - T_c$ with chirality (instead of the expected increase) is a consequence of these unrelated geometrical factors outweighing the more subtle effects of the twist energy.

On the other hand, the theory developed for the $I \rightarrow$ Ch transition may need modification in order to describe the $I \rightarrow$ BP transition. Such modification may improve agreement between theory and experiment as Atkinson and Collings have suggested [9].

4. Conclusions

The results discussed above extend the findings of earlier workers on COC and highlight the complexity of the temporal evolution of fluctuations even in the isotropic phase of BP-forming cholestogens. The temperature dependence of light scattering intensity that we observe with COC, however, is in good agreement with the report of Keyes and his coworkers even though their data spans only the low temperature region of our study.

Further theoretical effort ought, perhaps, to address the origin of the intricate light scattering correlation functions in the isotropic and pretransition region in BP-forming cholestogens as well as the nature of the $I \rightarrow$ BP transition itself. Experimental investigations of the influence of chirality upon phase transitions will have to recognize that unrelated molecular interactions may overwhelm more sensitive effects if mixtures, expecially of dissimilar substances, are used to modulate chirality. The use of neat compounds circumvents the problem of phase separation, but must contend with ill-characterized chemical variables; also, the pitch of the system may not be chosen at will in this protocol. Thus, the use of racemic mixtures of the same compound to effect changes in twist energy would appear to be especially well-suited to an investigation of the delicate interplay of forces in chiral systems.

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