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Optical activity of a side group cholesteric liquid crystalline silicone

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We measured, using a phase modulation technique, the optical rotation in the isotropic and blue phases of a side group cholesteric liquid crystalline silicone polymer. For comparison, similar measurements were performed on cholesteryl nonanoate (CN) and CE6. The polymer has a selective reflection close to that of CE6 and a chiral mesogenic side group chemically similar to CN. The optical activity data for the polymer, unlike those for low molecular mass liquid crystals, does not follow a simple Landau–de Gennes temperature dependence.

1. Introduction

Highly chiral nematics show complex pretransitional behaviour and form up to three blue phases (BPI, BPII and BPIII in order of increasing temperature). These phases are thermodynamically stable over a narrow interval (~ 1 K) and exist between the isotropic and the chiral nematic (cholesteric) phase. The helical structure of the cholesteric phase and the double twist configuration of the blue phase greatly enhance the optical activity (ϕ) of these phases. ϕ is also enhanced in the pretransitional isotropic region due to short range chiral order, but the optical activity in the isotropic phase is much less than that in the blue and cholesteric phases.

The theoretical basis for the unusually high optical activity of highly chiral nematics is now fairly well understood. One version of the Landau–de Gennes mean-field theory is based on the assumption that the order in chiral nematic liquid crystals can be represented by a linear combination of five basic structural modes [1, 2]. The modes labelled $m = \pm 2, \pm 1$ and 0 represent the planar spiral, conical spiral and the non-chiral modes, respectively (for illustrations of these structural modes see [3, 4]). Fluctuations of both the planar spiral and the conical spiral modes contribute directly to the optical activity [3, 5], with the conical spiral dominating, and without coupling between these modes as previously suggested [6]. Each mode has its own correlation radius and a characteristic temperature, T_m, at which this correlation radius diverges.

Apart from low molecular mass liquid crystals, the blue phase is also formed by side group oligomers [7, 8], side group polymers [9] and mixtures of chiral nematic liquid crystals and nematic polymers [10, 11]. In a polymeric liquid crystalline phase, the polymer backbone and the mesogenic units have antagonistic tendencies. The polymer backbone is entropically driven towards a random coil type configuration, while the mesogenic units stabilize with long range orientational order. The applicability of the present theory to chiral polymers which form blue phases remains untested. Consequently, we examine the optical activity in the isotropic and blue phase of a chiral liquid crystalline polymer.

2. Theory

The theoretical fundamentals of optical activity have been treated in detail elsewhere [4–6, 12–16]. We will therefore only present the results established by these studies. Plane polarized light travelling through an optically active medium of thickness z will be rotated through an angle ϕ:

$$\phi = \phi_0 + \phi_{m=\pm 1} + \phi_{m=\pm 2}. \qquad (1)$$

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ϕ_0, the molecular optical activity, is independent of orientational order and is given by:

$$\phi_0 = \frac{16\pi^3 N z \beta}{\lambda^2 c} \tag{2}$$

where β is the optical rotatory parameter, N the number density, λ the wavelength of light and c the vacuum velocity of light.

The structural optical activity, which is much greater than the molecular contribution, appears as soon as orientational correlations exist. The contribution to ϕ from the $m = \pm 1$ modes is given by:

$$\phi_{m=\pm 1} = \frac{k_{\mathrm{B}} T k_0^2 q_0}{48\pi \langle \varepsilon \rangle (a_0 b)^{0.5}} \left[1 + \frac{c}{2b} \right]^{-1.5} \frac{1}{(T - T_1^*)^{0.5}} \tag{3}$$

where k_{B} is the Boltzmann constant, k_0 the wave vector of the light, $\langle \varepsilon \rangle$ the average dielectric constant, and q_0 represents the chirality of the system ($q_0 = 4\pi/\mathrm{Pitch}$). a_0, b and c are the coefficients of the quadratic terms of the Landau–de Gennes free energy.

The contribution to ϕ due only to the $m = \pm 2$ modes is given by:

$$\phi_{m=\pm 2} = \frac{k_{\mathrm{B}} T k_0^2 q_0}{48\pi \langle \varepsilon \rangle (a_0 b)^{0.5}} \left[1 + \frac{c}{2b} \right]^{-1.5} \frac{1}{(T - T_2^*)^{1.5}}. \tag{4}$$

Equations (3) and (4) are consistent with experimental data except when applied to materials of very high chiralities (pitch $\lesssim 200\,\mathrm{nm}$). For such short pitched materials, Demikov and Dolganov [5] have predicted a temperature dependence of ϕ given by the expression:

$$\phi(T) = \frac{A}{(T - T_1^*)^{0.5}} + \frac{B}{(T - T_1^*)^{1.5}} + \frac{C}{(T - T_2^*)^{1.5}} + \phi_0. \tag{5}$$

The second term in equation (5) represents a higher order contribution to ϕ due to the $m = \pm 1$ modes. Unfortunately, only partial details of the calculations are given in [5]. The pretransitional optical activity of CB15 (pitch ~ 150 nm; Merck (UK) Ltd.) follows closely that of equation (5) [17]. However, owing to the large number of fitting parameters involved, the error estimates of some of the parameters can be quite high.

The Landau mean field description replaces a fluctuating local order parameter by a spatially averaged nematic alignment tensor. This is a good approximation if fluctuations of the order parameter about its mean are small. Recent theoretical [18] and experimental [19] studies establish that the phase transition line between the BPIII and the isotropic liquid phase ends at a critical point; this was first proposed by Koistinen and Keyes [20]. Englert *et al.* [21] show that fluctuations dominate the phase diagram of chiral nematic liquid crystals and cannot be ignored.

The mean field approach appears to be adequate for systems of low to moderate chirality, but is expected to break down close to the isotropic–BPIII critical point. Anisimov *et al.* [22] deduce from a careful analysis of the critical point that the closer one gets to it, the more the optical activity (and other physical properties) deviate from mean field dependences. Their analysis also predicts a pretransitional maximum in ϕ if the system is close enough to the critical point. Hence, deviations from mean field behaviour are expected in blue phase systems of very high chirality.

3. Experimental

We used a phase modulation technique (described in detail in [17]) in order to measure the temperature dependence of the optical activity. An Instec MK1 temperature controller which is accurate to ± 5 mK provided temperature control. The optical rotation angle was measured to ± 0.01° with a lock-in amplifier (EG&G Model 5104). The sample was heated into the isotropic phase, allowed to equilibrate overnight and then cooled slowly. Temperatures were decreased in desired steps and kept fixed for 15 min before any measurements were taken. This time interval far exceeded the time required for data acquisition (~ 1 s). Transitions were marked by discontinuities in either ϕ or the transmitted intensity or both.

The chemical structures of the materials used are illustrated in figure 1. The side group polymer has a siloxane backbone to which are attached both nematic and cholesteric mesogenic groups in approximately equal portions. For comparison, we performed optical activity measurements on two chiral nematics: (*S*)-4-(2-methylbutyl)phenyl 4-*n*-decyloxybenzoate (CE6) and cholesteryl nonanoate. CE6 was chosen because it has a cholesteric pitch which is similar to that of the polymer, while CN is structurally similar to the mesogenic moiety which is attached to the polymer backbone. The cholesteric silicone polymer is available from Wacker, CN from Kodak and CE6 from Merck (UK) Ltd. The samples were used without further purification.

4. Results and discussion

The temperature dependence of the pretransitional optical activity for the chiral polymer is shown in figure 2. ϕ decreases slightly until ~ 0.5 K above T_{c} and then increases rapidly, but remains positive throughout. This pretransitional divergence of the optical activity of the polymer is much smaller than that typically associated with low molecular mass chiral nematics [4, 13, 14, 17, 23–26]. Optical activity and light scattering data reveal that

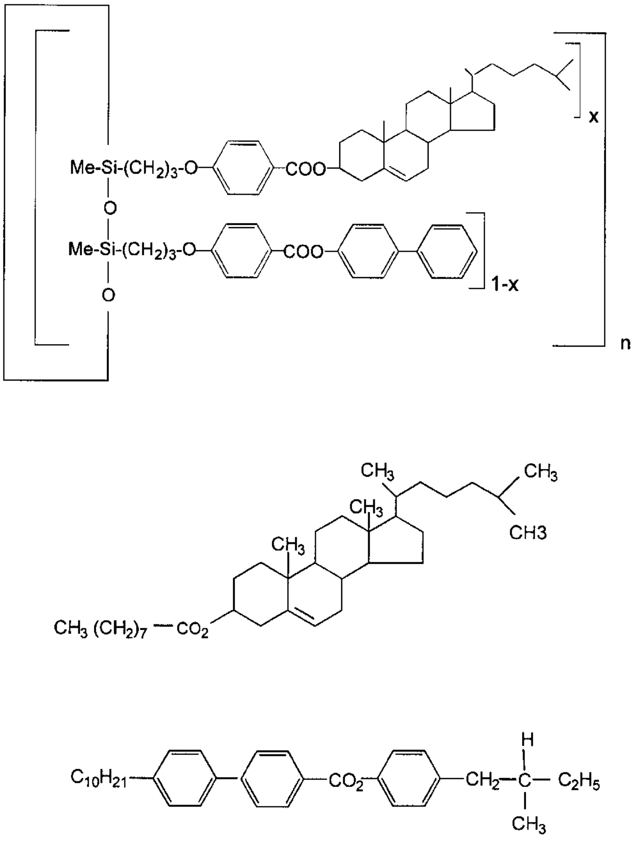

Figure 1. Chemical structures of the materials used in this study. Top: cholesteric silicone polymer, $x \approx 0.5$ and $4 \leqslant n \leqslant 8$; centre: cholesteryl nonanoate; bottom: CE6.

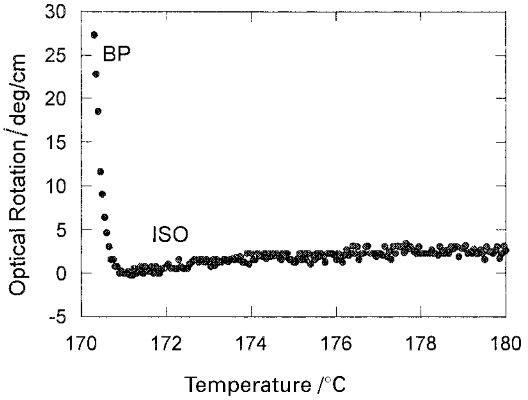

Figure 2. Pretransitional optical activity of the cholesteric liquid crystalline silicone. The wavelength of the light used was 633 nm and the sample cell had a 1 cm path length; temperatures were decreased in steps of 0.05 K. The complete BP region is not shown.

short range chiral order in highly chiral nematics can appear even as high as 10 K above T_c [3, 27]. A pretransitional extremum appears in the data, but it is not very pronounced.

The least squares fit to the pretransitional optical data using a combined $(T - T_1^*)^{-0.5}$ and $(T - T_2^*)^{-1.5}$ temperature dependence is shown in figure 3. The fit is not improved by the inclusion of the higher order $m = \pm 1$ term. The data in the high isotropic region are consistent with theoretical predictions, but there are significant deviations in the region ~ 2 K above T_c. The data follow a combined $(T - T_1^*)^{-0.5}$ and $(T - T_2^*)^{-1.0}$ temperature dependence, but there is no theoretical basis for such a fit.

The optical activity of the isotropic and the three blue phases of CE6 is shown in figure 4. ϕ reaches a maximum just above T_c, and then decreases. This maximum was not detected by Khan and Dunmur [4] but they decreased temperatures in much larger steps (~ 0.25 K).

Figure 5 shows the result of fitting the data to equation (5). The fitting parameters found are: $A = 4.7 \pm 0.3$ ($°\mathrm{C}^{1/2}\,\mathrm{cm}^{-1}$); $B = 26.3 \pm 3.9$ ($°\mathrm{C}^{1.5}\,\mathrm{cm}^{-1}$); $\phi_0 = -1.3 \pm 0.2$ (deg, cm^{-1}); $C = -19.3 \pm 4.0$ ($°\mathrm{C}^{1.5}\,\mathrm{cm}^{-1}$); $T_2^* = 44.43 \pm 0.4$ (°C); $T_1^* = 44.31 \pm 1.0$ (°C).

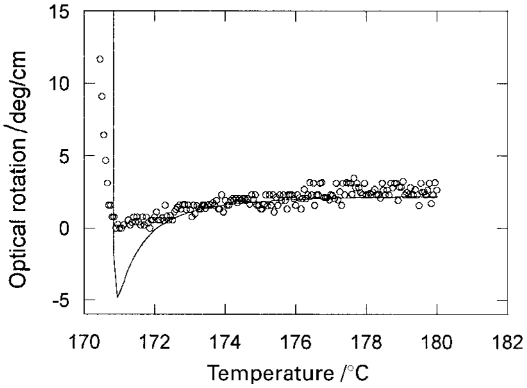

Figure 3. Theoretical fit to the pretransitional optical activity of the chiral polymer if a combined $(T - T_1^*)^{-0.5}$ and $(T - T_2^*)^{-1.5}$ temperature dependence is used. The circles represent the experimental data.

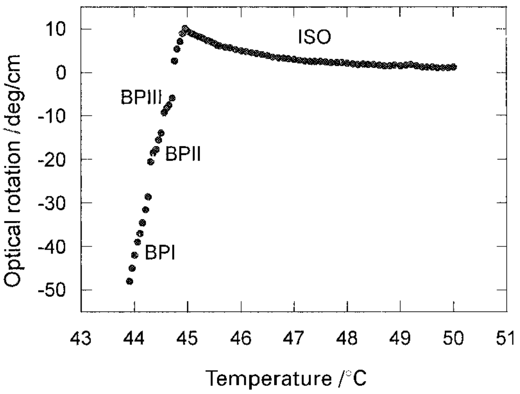

Figure 4. Optical activity in the isotropic and blue phases of CE6. The wavelength of the light was 633 nm and the path length of the cell 1.78 ± 0.01 mm. Temperatures were decreased in steps of 0.05 K.

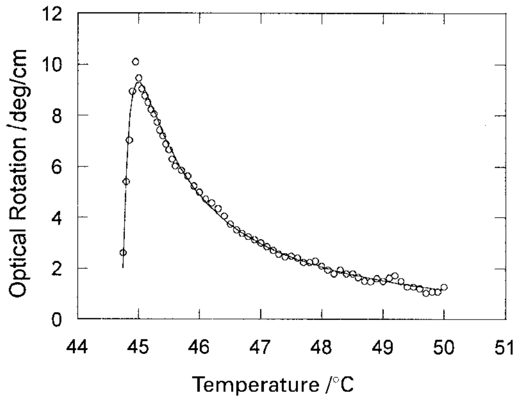

Figure 5. Theoretical fit of equation (4) to the optical activity (solid line) of the isotropic phase of CE6. The circles represent the experimental data.

Since the magnitudes of B and C are similar but of opposite signs, contributions from the second and third terms of equation (5) essentially cancel each other at temperatures much higher than the isotropic–BPIII transition temperature. The least squares fit is quite good except in the immediate vicinity of the pretransitional maximum where there is an 8% difference between theory and experiment. However, at higher temperatures, the data are quite consistent with mean field predictions.

The optical activity in the isotropic and blue phases of CN is shown in figure 6. CN forms three blue phases but it is difficult to identify BPII clearly since the BPII temperature interval is 80 mK and the latent heat of the BPIII–BPII transition is only 2 J mol^{-1} [28]. A pretransitional maximum in ϕ has been observed by Demikov and Dolganov [13] but not by Atkinson and Collings [26]. The maximum in ϕ which appears in our data (CN) is not as well defined as that observed for CE6, but CE6 has a shorter pitch than CN—160 nm [29]and 235 nm [13], respectively. The data follow a $(T - T_1^*)^{-0.5}$ dependence high above the transition temperature, but deviations are seen close to the transition temperature (see figure 7).

For chiral nematics, the sign of ϕ in the isotropic phase depends only on the intrinsic chirality. In the blue phase on the other hand, the sign of ϕ depends on whether the product nP (refractive index times pitch) is greater or less than the wavelength of the incident light (633 nm) [8]. ϕ changes sign at the isotropic–blue phase transition only if $\lambda > nP$. The Bragg reflections (nP) for these materials are all less than the wavelength of the incident light. These reflections are 460, 450 and 360 nm for CE6, the polymer and CN respectively [30–32].

The change in sign of ϕ at the isotropic–blue phase transition is obvious for the liquid crystals. The polymer data are similar to those for CN and CE6, except that all of it appears to be shifted to small positive angles and hence no corresponding change of sign is seen. This effect may be unique to cholesteric liquid crystals and due possibly to the restrictive effects of the polymer backbone. The polymer backbone is devoid of chiral centres, but it can still affect the optical activity indirectly, since there is direct competition between the chiral side group and the polymer backbone. The exact nature of the interactions between the side groups and the polymer backbone is still an open question. The effect of the length of the polymer backbone and the nature of the spacer on pretransitional fluctuations will be explored in the near future.

The temperature range of the single blue phase of the polymer is about 5 K. This range is consistent with that deduced from direct observations by polarizing optical microscopy. The optical activity of the blue phase of the polymer increases linearly with decreasing temperature and reaches a value of almost 600 deg cm^{-1} at the BP–cholesteric transition (see figure 8).

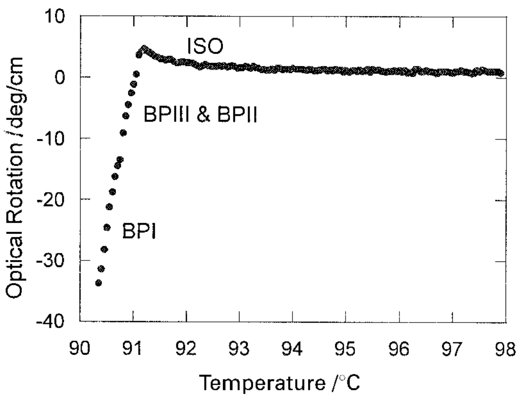

Figure 6. The optical activity in the isotropic and blue phases of CN. The wavelength of the light was 633 nm and the path length of the cell is 1 cm. Temperatures were decreased in steps of 0.05 K.

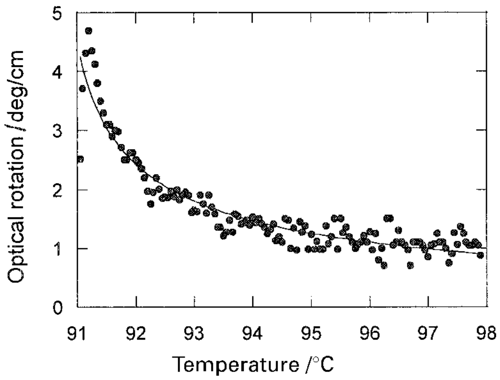

Figure 7. Theoretical fit to the optical activity (solid line) of the isotropic phase of CN. The circles represent the experimental data. The optical activity is fitted to a $(T - T_1^*)^{-0.5}$ temperature dependence. The addition of the last two terms in equation (5) did not improve the fit.

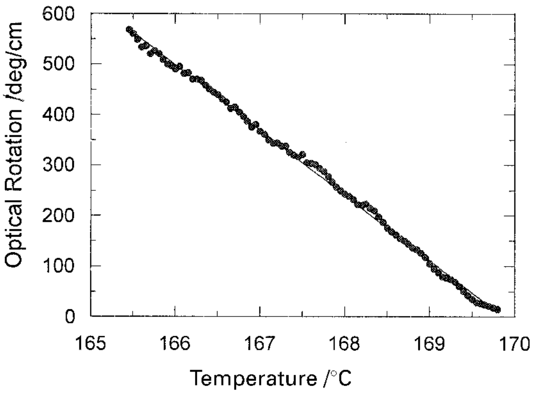

Figure 8. The optical rotation of the blue phase of the polymer. The wavelength of the light used was 633 nm and the path length of the cell 1.05 ± 0.01 mm. Temperatures were decreased in steps of 0.05 K.

5. Conclusion

For low molar mass liquid crystals, the mean field description appears to be adequate in the high isotropic region, but slight deviations near the isotropic–blue phase transition are obvious. The polymer data are similar to those for CN and CE6, except that all of the data appear to be shifted to small positive angles. The polymer showed much greater deviations from theoretical predictions than did the low molar mass liquid crystals. The present version of the theory appears to be inadequate when applied to polymers which form blue phases and modifications to it must take into account the influence of the polymer backbone.

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