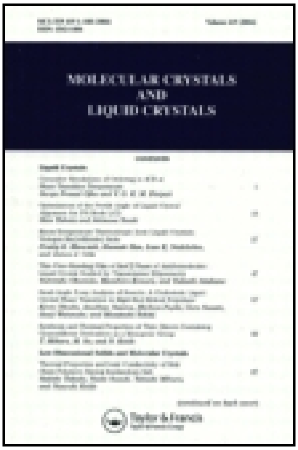

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Light Scattering Studies on a Siloxane Polymer-Chiral Nematic Liquid Crystal Blend

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Dynamic light scattering experiments using circularly polarized light in the back-scattering configuration were used to study the effect of polymer stabilization on the amplitude of fluctuations in two of the five structural modes present in the isotropic phase of the chiral nematic liquid crystal (S)-(+)-4-(2-methyl-butyl) phenyl 4-decyloxybenzoate (CE6). From these data, the second-order transition temperatures of these modes, which grow further apart if chirality increase were determined. When the chiral liquid crystalline polymer was added, the fluctuations of the modes deviated from the normal temperature dependence and the separation of the second-order transition temperatures increased.

Keywords: chiral nematic liquid crystal; dynamic light scattering; polymer-liquid crystal blend

INTRODUCTION

The macroscopic order parameter associated with phase transitions of chiral nematic liquid crystals is normally taken to be the anisotropic part of the dielectric tensor, $\mathbf{Q}_{\alpha\beta}(\mathbf{r})$. This tensor being symmetric and traceless can be represented in terms of five independent structural modes [1–3]; all of which can fluctuate about their equilibrium value at a finite temperature. These modes labeled m = ±2, ±1 and 0 represent the planar spiral, conical spiral and achiral modes respectively (see [4,5] for illustrations of these modes). The landau-de Gennes free energy for each of these modes vanishes at some temperature T_m^*. All T_m^* are lower than the transition temperature, T_c, and $T_2^* > T_1^*$.

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The most direct way to measure fluctuations in the isotropic phase is to perform light scattering experiments. By using the Mueller matrix formalism, Hornreich and Shtrikman [6] have derived a general scattering matrix in terms of the amplitudes of the five modes and the scattering angle. In this approach, the input and output beams are expressed as 4 × 1 Stokes vectors. The connection between the two vectors can be expressed as a linear transformation whose sixteen coefficients form the 4 × 4 Mueller matrix from which all scattering properties of the sample can be determined.

In general, light is scattered from a combination of the five modes of the order parameter. However, a single mode can be probed by employing the back scattering of right (or left) circularly polarized light [R(L)CPL]: all other scattering geometries are sensitive to the fluctuations of more than one mode. If both incident and back-scattered beams are RCPL (LCPL) the $m = -2$ $(m = +2)$ mode is excited and there is no contribution from the $m = \pm 1$ modes [6]. If the incident beam is RCPL (LCPL) and the back-scattered beams are LCPL (RCPL), coupling with the $m = 0$ modes occur. From such experiments, one can deduce the 2nd order transition temperatures, T_m^*.

THEORY

For a cholesteric liquid crystal, the Landau-de Gennes free energy to second order can be written as [6–8]:

$$F_2 = F_0 + \frac{1}{2}\int d\vec{r}\Big[aQ_{\alpha\beta}^2 + b\left(\partial_\gamma Q_{\alpha\beta}\right)^2 + c\partial_\alpha Q_{\alpha\gamma}\partial_\beta Q_{\beta\gamma} - 2de_{\alpha\beta\gamma}Q_{\alpha\delta}\partial_\gamma Q_{\beta\delta}\Big] \tag{1}$$

where $Q_{\alpha\beta}$ is the dielectric tensor representing the local order, $e_{\alpha\beta\gamma}$ is the Levi-Civita tensor, $a = a_0(T{-}T^*)$, the coefficients b, c and d are temperature independent and T^* is the second order phase transition temperature of the racemic mixture. If the order parameter is expressed in terms of the five structural modes, Eq. (1) reduces to:

$$F_2 = F_0 + \frac{1}{2}\sum_m \int d^3\vec{q}\left[a - mdq + \left[b + \frac{c}{6}\left(4 - m^2\right)\right]q^2\right]|\sigma^m(\vec{q})|^2 \tag{2}$$

where m labels the mode, $\vec{q}$ is the wave vector of light and $\sigma^m(\vec{q})$ is the amplitude of the mode. There is a specific value of q, which minimizes the free energy of each mode.

By using the equipartition theorem, the mean-square fluctuation of the modes can be written as:

$$\langle \sigma^m(\vec{q})\sigma^m(-\vec{q})\rangle = \delta_{\vec{q},-\vec{q}}\frac{(k_BT)/2}{\tau^m(\vec{q})} \tag{3}$$

where,

$$\begin{aligned} \tau^{\pm 2}(q) &= a + bq^2 \mp 2dq \\ \tau^{\pm 1}(q) &= a + (b+c)q^2 \mp 2dq \\ \tau^{0}(q) &= a + \left(b + \frac{2}{3}c\right)q^2 \end{aligned} \tag{4}$$

Following Hornreich and Shtrikman, one can deduce expressions for the scattered intensity in any one of the four possible scattering configurations. For RCPL incident and RCPL detected, the intensity is given by:

$$I(\vec{q}) = \frac{k_BT}{2}\left[\frac{2c^4}{3\tau^0} + \frac{(1-s)^4}{\tau^2} + \frac{(1+s)^4}{\tau^{-2}}\right] \tag{5}$$

where θ is the scattering angle, $s = \sin\frac{\theta}{2}$ and $c = \cos\frac{\theta}{2}$.

For LCPL incident and LCPL detected, a similar calculation yields:

$$I(\vec{q}) = \frac{k_BT}{2}\left[\frac{2c^4}{3\tau^0} + \frac{(1+s)^4}{\tau^2} + \frac{(1-s)^4}{\tau^{-2}}\right] \tag{6}$$

If the incident and scattered beams have opposite states of polarization, the intensity is given by the expression:

$$I(\vec{q}) = \frac{k_BT}{2}\left[\frac{2(c^2+2)^2}{3\tau^0} + \frac{4c^2}{\tau^1} + \frac{4c^2}{\tau^{-1}} + \frac{(s^2-1)^2}{\tau^2} + \frac{(s^2-1)^2}{\tau^{-2}}\right] \tag{7}$$

For the scattering angle used in this experiment, $\theta = 175^\circ$, the coefficients of the first and second terms in Eq. 5 are 1.5×10^{-7} and 5×10^{-14} times that of the third term respectively. Thus, for a right handed system, the contribution of the $m = -2$ mode to the backscattering is much greater than that of either the $m = 2$ or $m = 0$ mode. The situation is reversed for a left-handed system. According to equation 3, the scattered light intensity should vary as $[T - T^*_{\pm 2}]^{-1}$ in the isotropic phase. Thus, a plot of inverse intensity versus temperature should be linear with the intercept along the temperature axis being $T^*_{\pm 2}$.

EXPERIMENT

The optical system (Fig. 1) was designed to measure fluctuations from just one mode. Circularly polarized light was generated by passing horizontally polarized light (from a He-Ne laser) through a quarter-wave plate ($\lambda/4$) whose fast axis was oriented at 45° to the x-axis (-45° yields LCPL and $+45^\circ$ yields PCPL). The incident light was focused onto the sample by using a long focal length convex lens. The back-scattered beam is a mixture of RCPL and LCPL since it contains contributions from the sample as well as reflections from nonchiral materials. For example, RCPL is reflected as LCPL from glass. This mixture of RCPL and LCPL was decomposed into two orthogonal polarized beams with the help of a second quarter wave plate whose orientation is the same as the first. LCPL (RCPL) was then detected by passing the light through a horizontal (vertical) polarizer.

The apparatus is fully automated. Correlation functions were measured by a BIC 9600AT correlator board, which is mounted in computer 1 (MC1). Both quarter-wave plates and the Instec MK1 temperature controller were interfaced to computer 2 (MC2). The transmitted light was fed into a digital multimeter (TES 2730 Model). Intensity changes generally indicate where transitions are occurring. Microcomputers 1 (MC1) and 2 (MC2) were interfaced for data acquisition.

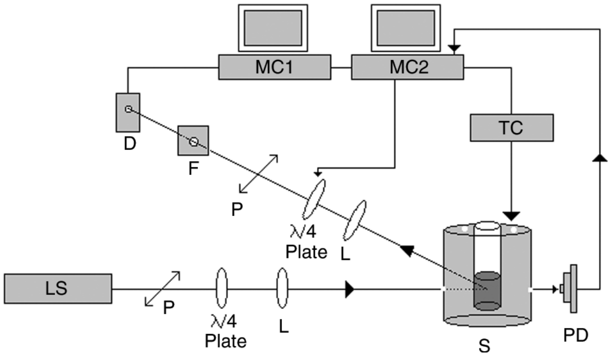

FIGURE 1 The scattering geometry which was used to detect fluctuations from a single mode. The symbols are: LS (Light source): P (Polaroid): $\lambda/4$ plate (Quarter wave plate): L (Lens): F (Filter): D (Detector): MC (Microcomputer): TC (Temperature controller): S (Sample): PD (Photodiode).

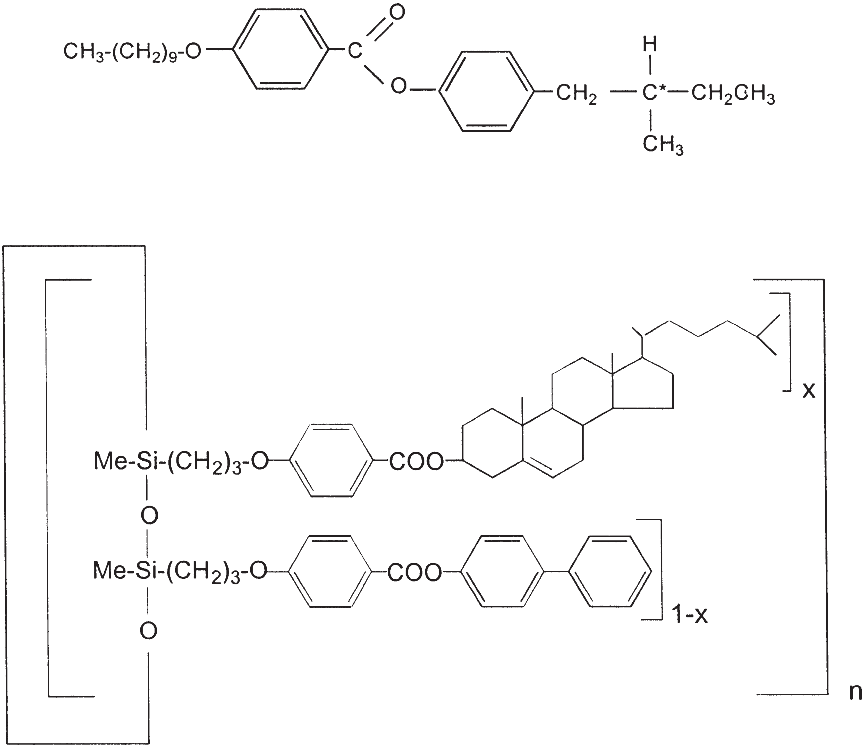

FIGURE 2 Chemical structures of the materials used in this study. Top: (S) – (+)-4-(2–methyl-butyl) phenyl 4-decyloxybenzoate (CE6); bottom: cholesteric silicone polymer (C4745) $x \approx 0.5$ and $4 \leq n \leq 8$.

The chemical structures of the materials used are shown in Figure 2. The mesophase range of the polymer (C4745) is from ~65–183°C [9]. It forms a single blue phase whose range is ~5°C while CE6 forms three blue phases (~1°C range).

The blend was prepared by dissolving the mixture in dry dichloromethane. The solution was then allowed to evaporate at room temperature. All remaining solvent was removed by drying the sample at 50°C for 24 hours. During the experiment, the sample was heated to ~25°C above T_C and allowed to equilibrate in order to determine the background intensity. Similar equilibration at ~10°C above T_C was performed before data were collected. Readings of correlation function, scattered intensity and temperature were recorded at 0.05°C intervals. The cooling rate was 0.5°C h^{-1}. The procedure was repeated for the polymer-doped sample.

RESULTS AND DISCUSSION

A plot of inverse intensity versus temperature in the isotropic phase of pure CE6 is shown in Figure 3. The solid lines are least squares fit to the expression:

$$I = K\left[T - T^*_{\pm 2}(q)\right]^{-1} + I_0 \tag{8}$$

where I is the backscattered intensity, and K, $T^*_{\pm 2}$(q), and I_0 are fitting parameters. The two graphs show the same T_C but different T^* (given by the intercepts on the temperature axis). Hence there is good correlation between theory and experiment. For CE6, T_C, $T^*_{-2}$and T^*_{+2} are 45.20, 44.72 and 44.27 (temperatures are in °C and are accurate to ±0.01°C). Wyse and Collings [10] have found that that the difference in the second order temperatures (T^*_{-2}–T^*_{+2}) even in highly chiral systems is usually less than a degree. The fluctuations in the "strongest" and "weakest" modes in CE6 differ by a factor of ~2 just above T_C and less than this at higher temperatures. Also, the helix in CE6 is right-handed.

The phase sequence of the siloxane polymer as deduced from DSC is [9]:

$$Cryst \xrightarrow{65} N^* \xrightarrow{178} BP \xrightarrow{183} Iso$$

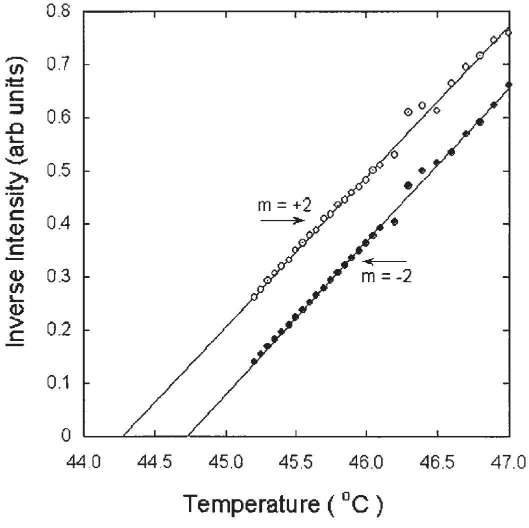

FIGURE 3 Reciprocal of the backscattered intensity in the isotropic phase of CE6.

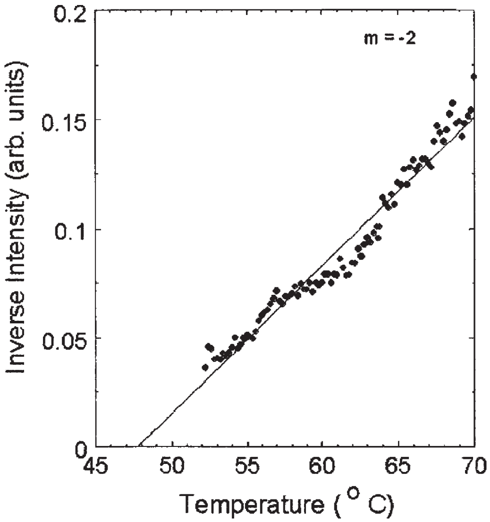

FIGURE 4 Reciprocal of the backscattered intensity for the two scattering configurations for 90% CE6/10% polymer.

Performing scattering at temperatures corresponding to the isotropic phase of the polymer is beyond the scope of our apparatus and hence we could not determine the handedness of the helix in C4745. The inverse intensity for each scattering mode in the polymer-doped sample is plotted separately (for clarity) in Figure 4. As expected, the blend scattered considerable more light that the pure liquid crystal. Both plots are linear except for a central region of ~5°C. This region corresponds to the crystallization of the polymer and is marked by a discontinuity in the data. Also, at temperatures just above T_C(~53°C), the data deviates slightly from a linear dependence.

At temperatures >65°C, the back–scattered light is made up of contributions from the cholesteric phase of the polymer and the isotropic phase of the liquid crystal. The order in the cholesteric phase can be represented by a combination of the m = 0 and m = ±2 modes with the dominant contribution coming from the m = ±2 modes. Thus, the high temperature linear region of each plot represents contributions almost entirely from the polymer since there is little or no scattering from CE6 at these temperatures. Hence, the theory appears to be valid in the cholesteric phase of the polymer. The linear region at the low temperatures end of the plot extends for ~7°C (about twice the range of pure CE6). Unlike pure CE6, T^*_{+2} is greater than T^*_{-2} in

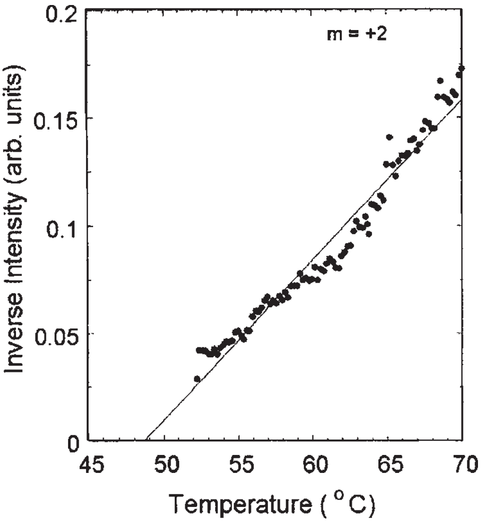

FIGURE 5

the polymer blend. This may mean that the helix in C4745 is left-handed.

The difference in the second order transition temperatures is ~1.05°C for the polymer blend and 0.45°C for the pure CE6. This difference is even greater if the fit is for just for $T < 60°C$. This increase in (T^*_{+2}–T^*_{-2}) which is associated with an increase in chirality is unexpected since this small amount of polymer is not expected to change the chirality of the liquid crystal significantly. However, the polymer may affect the liquid crystal indirectly since the polymer backbone has a tendency to form a random coil while the mesogenic units stabilize with long-range orientational order.

CONCLUSION

We have shown that it is possible to scatter from the fluctuations of a single mode and hence determine the second-order phase transition temperatures $T^*_{\pm 2}$. For the pure material, the experimental results are consistent with theoretical predictions. However, scattering from the blend appears to be complex and outside the scope of the present theory. The polymer and the liquid crystals are probably immiscible since the polymer crystallizes at approximately the same temperature in the blend as well as in the pure material.

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