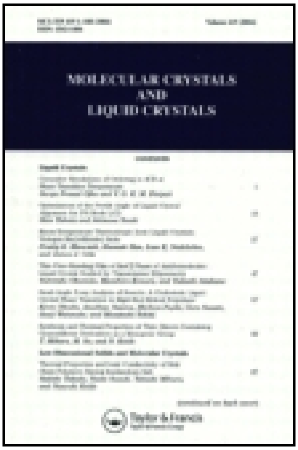

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THERMAL, OPTICAL AND ELECTRO-OPTICAL PROPERTIES OF A CHOLESTERIC SIDE-CHAIN POLYMER WITH A SILOXANE BACKBONE

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Thermal, Optical and Electro-Optical Properties of a Cholesteric Side-Chain Polymer with a Siloxane Backbone

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The fundamental thermal and optical properties of a side-chain cholesteric liquid crystal silicone, which forms a single blue phase, were investigated. In particular, we examined the optical activity of the isotropic and blue phase for fields varying from zero to approximately 10^6 Vm^{-1}. The zero-field optical activity data is not consistent with theoretical predictions. Optical microscopy, Bragg reflections and thermal analysis were also used to further characterize the properties of the liquid crystalline phases.

Keywords: optical activity; DSC; Bragg reflections; side-chain polymer

INTRODUCTION

Side-chain liquid crystal polymers combine the characteristic features of classical polymers with the rich phase behaviour order of low molecular mass liquid crystals. They consist of three main structural units: the polymer backbone, the mesogenic unit and the spacer-chain, which attaches the mesogenic unit to the polymer backbone. The polymer backbone, which is entropically driven towards a random coil configuration, opposes orientational order of the mesogen. Hence, spacer chains must be long enough[1,2] to allow orientational order to persist in-spite of steric constraints imposed by the polymer backbone.

Recent experimental work[3-5] has demonstrated that the thermodynamic fluctuations, which take place near transitions in chiral liquid crystals, display a richness not present in non-chiral systems. These fluctuations[6] can be quite strong with complex temperature and wavelength dependence. Highly chiral polymers are also expected to display unusual pretransitional effects, possibly some not seen in low molar mass liquid crystals. Hence, cholesteric liquid crystalline silicones are suitable candidates for fundamental study. We focus on the basic optical and thermal properties of a chiral side-chain polymer, which forms a blue phase.

EXPERIMENT

The chiral polymer (4745) shown in figure 1 is a cyclic siloxane-based side chain polymer. The silicon atoms of the ring vary from 4 to 8. Chiral (cholesterol derivative) and non-chiral mesogens are attached in an alternating sequence to the polymer backbone by flexible spacers. The material (Wacker) was used as obtained.

We used a rotating analyzer system (described elsewhere[7]) to measure the optical activity to ± 0.01°. Thermograms were obtained with a Seiko SSC/5200 DSC, which is equipped with a heating unit and nitrogen circulation. The heating and cooling rates were 10° C/min. For Bragg reflections, light from a polarizing microscope operating in the reflecting mode was diverted into a monochromator. The reflection spectrum was deduced from the output of a photomultiplier tube, which was placed at the exit slit of the monochromator.

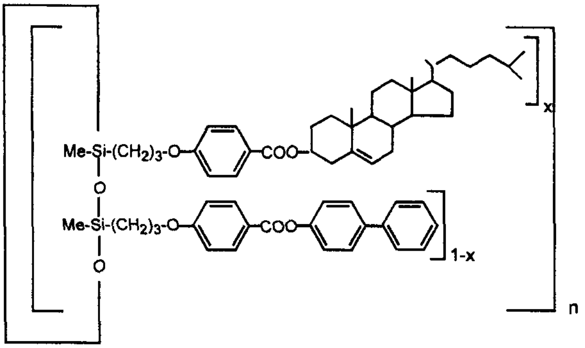

FIGURE 1 The chemical structure 4745: x~ 0.5 and 4 ≤ n ≤ 8.

RESULTS AND DISCUSSION

Thermal Analysis

Thermal analysis reveals a broad liquid crystalline range of ~ 120 °C (see table 1). T_g, T_m and T_{cl} are the glass, melting and clearing transitions respectively; ΔH is the corresponding latent heat.

The clearing transition is a weak first-order transition, which is accompanied by hysteresis. T_{cl} obtained if the sample is cooled is about 10 °C lower than when it is heated. The cooling curve does not show a freezing transition. This could be the result of too rapid cooling or the formation of a glassy state.

	T_g (C) / ΔH (J/g)	T_m (C) / ΔH (J/g)	T_{cl} (C) / ΔH (J/g)
Heating	53.1 / 0.3	57.6 / 5.5	180.6 / 3.2
Cooling	-	-	170.7 / 0.9

TABLE 1 Transitions of 4745 deduced from DSC.

Peaks corresponding to the blue phase of 4745 were absent from DSC scans. However, the blue phase readily forms if the sample is allowed to equilibrate close to T_{cl} for at least 24 hrs and then cooled at a rate, which maintains equilibrium. Under such conditions, the blue phase is stable over a range of ~ 5 °C. Transition temperatures deduced from DSC were used as a guide for the optical characterization of the material.

Optical Activity

If plane polarized light is incident on an optically active material, it emerges with its plane of polarization rotated through some angle. An optically active material lacks a centre of symmetry. Theoretical fundamentals of optical activity in chiral nematic liquid crystals are now fairly well understood and this subject is treated in several places[8-12]. The pretransitional optical activity (ϕ) is due to short-range chiral order which develops close to the isotropic-blue phase transition (T_c). The double twist configuration of the blue phase and the helical structure of the cholesteric phase enhance the optical activity in these phases. Hence, the optical activity of the liquid crystalline phases is much greater than that of the isotropic phase.

If the chirality of a liquid crystal is not too high, the pretransitional optical activity follows a $(T - T^*)^{-0.5}$ temperature dependence, where T^* is a temperature slightly below T_c. For much higher chiralities, this temperature dependence is invalid and higher order terms are required[7-11]. The pretransitional optical activity of the polymer is shown in figure 2. The data does not follow the expected temperature dependence. Since the polymer backbone restricts orientational order, it is not surprising that the chiral polymer does not show the typical pretransitional divergence associated with liquid crystals[13,14]. Short-range chiral order in liquid crystals can develop even as high as 10 ° C above T_c. Instead, for 4745, ϕ decreases slightly until about 0.5 ° C above T_c and then increases rapidly. The optical activity is not consistent with mean field predictions even if higher order terms are considered. Also, similar to what is observed for highly chiral nematics, there is a maximum in ϕ[7] just before T_c.

The optical activity of the blue phase (see figure 3) is much greater than that of the isotropic phase but ϕ increases linearly with decreasing temperature. Chiral nematics show a change in sign of ϕ at the isotropic-blue phase transition if $\lambda > n\,p$ (pitch x refractive index). However, under similar conditions, the polymer does not show this sign change. The reason for this is unclear at present.

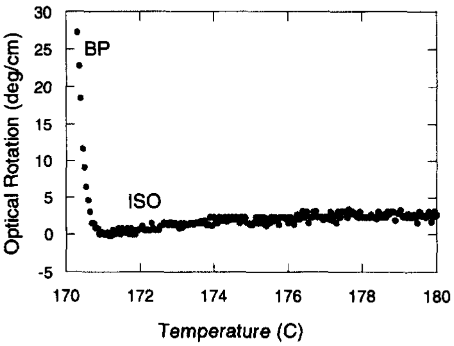

FIGURE 2 The optical activity of the isotropic phase of 4745. The wavelength is 633 nm and the sample thickness is 1cm. The entire blue phase is not shown. There is a discontinuity in ϕ at the isotropic-blue phase transition.

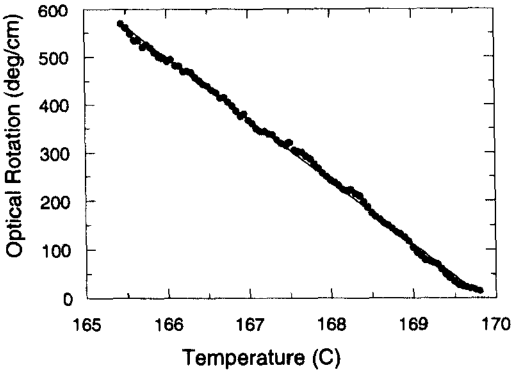

Figure 3 The optical activity of the blue phase showing a linear temperature dependence. Sample thickness is 1.05 ± 0.01 mm.

We also examined, on a preliminary basis, the effect of electric fields on the optical activity of the isotropic and blue phases of 4745. The optical activity of the isotropic and blue phase for 2000 V d.c. is shown in figure 4. The optical activity of both phases is greatly reduced. However, the optical activity of the blue phase still retains a linear temperature dependence. Other features include a slight increase in the isotropic-blue phase transition and a reduced temperature interval of the blue phase. These effects have been observed for chiral nematics[7]. We are quite aware that the application of d.c. fields represents a non-ideal condition since the build-up of charges reduce the effect of applied voltage. However, our a.c. source has a maximum output of 500V. When this a.c. field was applied, little or no effect on either the transition temperature or the stability of the blue phase was observed. In addition, 3000 V generated fields which destroyed the sample.

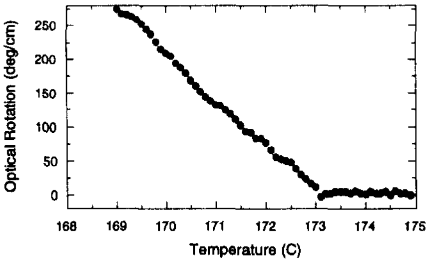

FIGURE 4 The optical activity of the isotropic and blue phases when 2000V (10^6 V/m) are applied.

Bragg reflections

The cholesteric pitch of chiral nematics is a fundamental quantity of interest to both experimentalist and theoreticians. We examined the temperature and wavelength dependence of Bragg reflections of the cholesteric phase. The results for a homogeneous (planar) aligned sample are shown in figure 5.

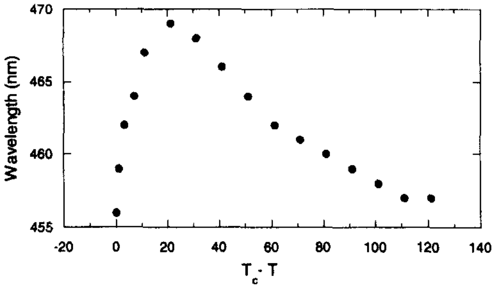

FIGURE 5 Temperature dependence for the Bragg peaks of the cholesteric phase of 4745

The Bragg reflection peaks of chiral nematic liquid shifts towards longer wavelengths if a sample is cooled but Bragg peaks of 4745 however, contain a maximum. Hence, interactions between the polymer backbone and the mesogens exist in the cholesteric phase even at fairly low temperatures. Similar experiments on the blue phase are planned for the near future.

CONCLUSION

We have examined the basic thermal and optical properties of a chiral nematic. These properties show deviations from those seen in liquid crystals. Even though the backbone is devoid of chiral carbon atoms it can still have a profound effect on the basic properties of the polymer since it influences orientational order of the mesogens. Present theories, which are useful for chiral liquid crystals, need to be extended for chiral polymers.

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