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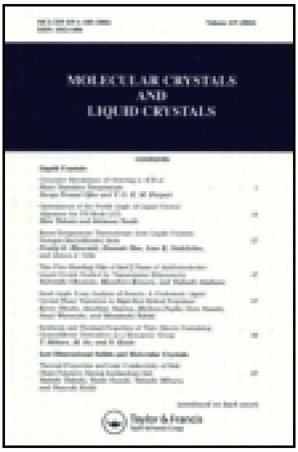

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THERMAL BEHAVIOUR AND ELECTRO-OPTIC PROPERTIES OF A NEMATIC EXHIBITING CYCLIC SILOXANE.

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Abstract The thermal behaviour of a homologous series of cyclic siloxane liquid crystals with cyanobiphenyl terminal groups and alkoxy linkages is presented. One member of this series, with an n=3 alkoxy spacer, exhibits a broad nematic phase and an above ambient glass transition. Excellent planar alignment was obtained in the nematic phase using low tilt rubbed polyimide, and uniform switching was seen on the application of a transverse electric field above threshold. Splay threshold voltages have been measured as a function of temperature and the splay elastic constant, K_{11}, calculated. For equivalent reduced temperatures, the splay threshold voltage and elastic constant for the cyclic - 3 OCB are similar to those for low molar mass 5CB. Electro-optic switching times and contrast ratios have been measured in a twisted nematic geometry. The effect may be stored below the glass transition.

INTRODUCTION

Low molar mass (LMM) cyanobiphenyl liquid crystals[1] are well known for their excellent electro-optic properties and have been extensively used in display applications. Side-chain liquid crystal polymers (SCLCP)[2], in which pendant mesogenic groups are attached via flexible spacers to a polymer backbone, are seen to exhibit similar electro-optic effects to their LMM analogues[3] and have been widely studied. The inclusion of the polymer backbone results in a broader mesophase range, a reduction of the tendency to from a crystal with preference for a glass phase, and a higher clearing temperature[4] in comparison to a LMM material. Polysiloxane SCLCPs with cyanobiphenyl pendant units are reported to exhibit interesting electro-optic and storage properties[5-7]. The siloxane backbone is highly flexible and in general presents a much lower glass transition temperature (Tg) than its polyacrylate or methacrylate equivalents. The polydispersity of the commercially available linear polysiloxane backbone has a strong influence on the transition temperatures and the response of the mesogenic groups to applied electric and magnetic fields, resulting at times in problems with reproducibility of physical properties between sample batches. Cyclic siloxanes with between 3 and 25 repeats, pendant mesogenic groups and low polydispersity have been reported to exhibit a wide range of

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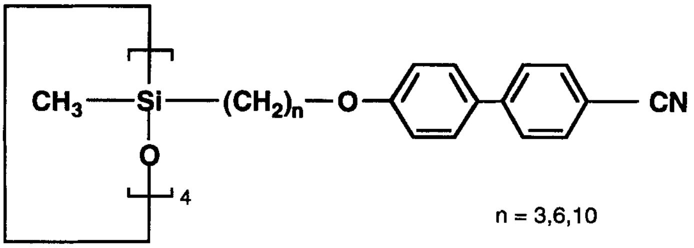
mesophases[8-14]. Such systems also have lower viscosity in the isotropic phase than comparable polymers leading to easier processability.

Cyclic liquid crystal siloxanes (CLCS) were first synthesised in 1981[8-9]. Studies to date have concentrated on systems incorporating cholesterol side groups[10-12] which have been utilised for optical data storage[15] and as optical notch filters[16]. Further to this, chiral side groups have been used to obtain ferroelectric mesophases and glasses with a view towards obtaining high χ^2 materials for use in non-linear optics (NLO) applications[13]. Thermal behaviour comparisons between cyclics and analogous linear polymers have yet to produce consistent trends: for example, there was little difference in transition temperatures between the cyclic and linear analogues of a cholesterol/biphenyl series[11], whereas for both cyanoester and cyanobiphenyl series, the cyclics exhibited higher clearing temperatures[14]. This indicates that CLCS systems are still of scientific interest and similarly seem to be increasingly important for potential applications.

In this paper we report on the thermal behaviour of a homologous series of cyclic siloxanes pendantly substituted with cyanobiphenyl groups via alkoxy spacers. The electro-optic characteristics of a nematic-exhibiting homologue of the above series have been measured and are presented. The thermal behaviour of such systems has previously been studied as a function of the cyclic ring size and comparisons made with equivalent linear systems[14]. However, cyclic siloxanes with biphenyl terminal groups synthesised to date predominantly incorporate ester linkages[10-12]. The current compounds were synthesised as part of a series of siloxane liquid crystals with cyanobiphenyl mesogenic units. The series consists of low molar mass systems with a monomesogenic BA[17-19] or bimesogenic ABA[19] structure (where A refers to the biphenyl unit and B refers to a dimethylsiloxane chain) and linear polymers[20] in addition to the cyclic systems. The mesophase behaviour and electro-optic properties of the smectic exhibiting members of the cyclic series will be presented in a further paper and comparisons will be made between the monomesogenic, bimesogenic, cyclic and polymeric analogues.

MATERIALS

The CLCS series studied were synthesised as described previously[21] and provided by Dow Corning (Barry, UK). No attempt at further purification was made. The chemical structure is shown below. In this paper we concentrate on the macroscopic properties of the nematic exhibiting, n=3 homologue with a four siloxane cyclic backbone.



EXPERIMENTAL

Thermal analysis was obtained using a Perkin Elmer DSC-7. Optical textures were observed using an Olympus BH-2 polarising microscope equipped with a Linkham TP91 heat stage.

Electro-optic characterisation was carried out using custom-made 7.5 μm glass cells (indium tin oxide electrodes, 25 mm^2 active area, rubbed polyimide alignment layer) and an optical microscope modified to house a photo diode detector. A field was applied across the cell in the viewing direction via a Thurlby-Thandar TG1304 Programmable Function Generator and home-made amplifier. Sample temperature and signal voltage and frequency were controlled by BBC computer. Response times were measured using a Hewlett Packard 54600A oscilloscope and a Wayne-Kerr 6425 Multi Bridge was used for dielectric constant measurements at 1 kHz.

RESULTS AND DISCUSSION

Thermal behaviour was determined by differential scanning calorimetry and polarising optical microscopy (Table 1). Structures were confirmed by x-ray diffraction.

substituent	phase behaviour					
3 OCB	G	54°C	N	109°C	2.7 J/g	I
6 OCB	G	57°C	Sm A	118°C	5.6 J/g	I
10 OCB	K	55°C	Sm A	134°c	9.7 J/g.	I

TABLE 1 Phase transition temperatures and enthalpies (DSC)

Cyclic - 3 OCB exhibits a broad enantiotropic nematic phase and an above ambient glass transition. Of the monomesogenic, bimesogenic, cyclic, polymer siloxane series studied this is the only nematic phase observed. The strong amphiphilic nature of the three components (siloxane, alkoxy spacer, cyanobiphenyl) which in the analogous linear systems results in a separation into distinct, single component smectic layers is partly

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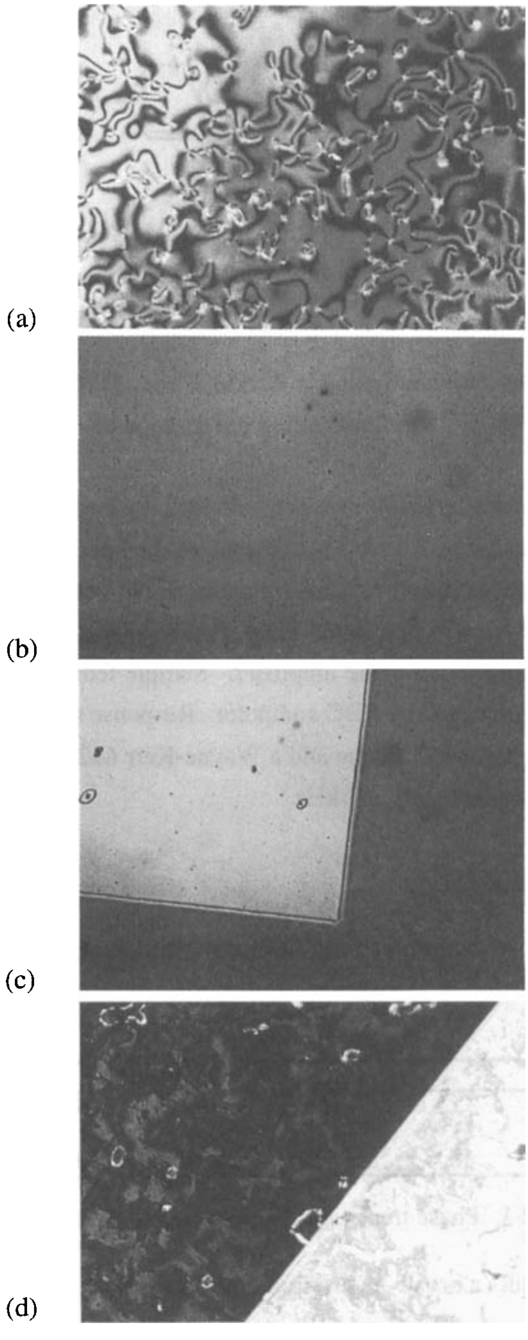

FIGURE 1 Observed optical textures for cyclic - 3 OCB between crossed analyser and polariser at a reduced temperature (T-T_{NI})of 10°C: (a) clean glass substrates, (b) low tilt, anti-parallel rubbed polyimide alignment layers, (c) as (b) on application of a transverse voltage of 3V, (d) in a twisted nematic geometry with the same applied voltage.

See Color Plate VIII.

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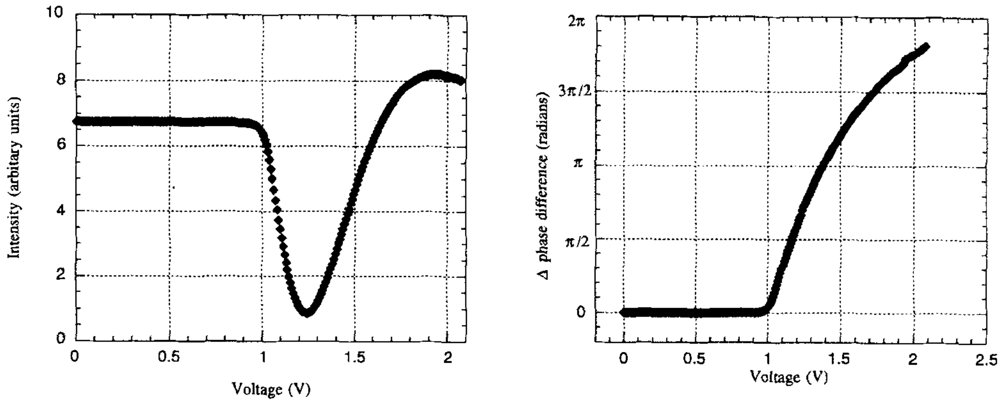

FIGURE 2 Typical transmitted intensity and phase difference response for cyclic - 3 OCB as a function of voltage in an AP geometry (see text).

overcome by the steric restriction due to the small ring and short spacers. A nematic phase has been predicted for small ring, short spacer CLCS[22,23], and observed in a number of other cases[11,12].

Good planar alignment was achieved using low tilt polyimide alignment layers with anti-parallel rubbing directions (AP). On application of an electric field above threshold a uniform change in birefringence was seen in the AP geometry (Figure 1b&c).

As a means of comparison between the cyclic system and a low molar mass nematic (4-cyano-4-5-alkyl biphenyl, '5CB'), the splay visco-elastic constants of the two compounds were measured. The threshold voltage for a splay deformation was measured as a function of temperature by recording the level of light transmitted through a cell on slow scan stepping of the voltage. Transmitted intensity (I) was converted into phase retardation via

$$I = I_0 \sin^2 (\delta/2),$$

and the threshold voltage (V_{th}) determined by extrapolating to $\delta = 0$ (Figure 2). Splay elastic constant values were calculated using the relationship

$$K_{11} = \Delta\varepsilon\, \varepsilon_0 V_{th}^2 / \pi^2$$

and are plotted in Figure 3. Dielectric anisotropy was calculated from measured values of $\varepsilon_{isotropic}$ and $\varepsilon_{perpendicular}$. V_{th} and K_{11} for 5CB were calculated in the same way giving

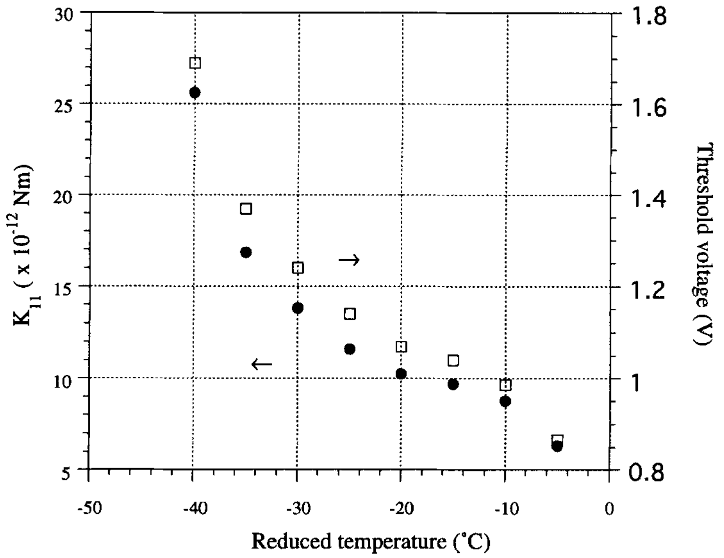

FIGURE 3 Threshold voltage and splay elastic constant, K_{11}, of cyclic - 3 OCB as a function c reduced temperature ($T-T_{NI}$).

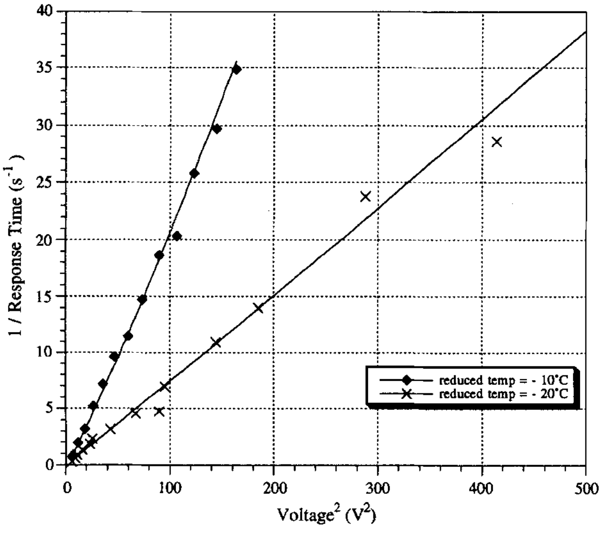

FIGURE 4 Response time dependence on applied voltage for cyclic - 3 OCB

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values of 0.72V and 4.9 x 10^{-12} Nm respectively (T_{red} = -5°C), which are in good agreement with values quoted in the literature[24]. For equivalent reduced temperatures, the splay threshold voltage and elastic constant for the cyclic - 3 OCB and are similar to those for low molar mass 5CB. At low temperatures, as T_g is approached, the splay elastic constant appears to diverge for the cyclic compound in contrast to the behaviour for 5CB which undergoes crystallisation at low temperatures.

The electro-optic switching time in a twisted nematic (TN) geometry was measured as a function of voltage for two reduced temperatures (Figure 4). As expected, 1/response time is linearly proportional to voltage[2]. Response times of 100ms were observed for operating voltages of <10V in the 7.5 µm thick cell. High contrast ratios (CR = 6 for 5V, 22 for 10V at 1 kHz) were recorded for the TN geometry (Figure 1d). The induced orientation could then be stored on cooling the sample below T_g to room temperature.

CONCLUSIONS

The thermal behaviour and electro-optic properties of a cyclic siloxane with cyanobiphenyl terminal groups and alkoxy linkages have been presented. The compound exhibited a broad enantiotropic nematic phase whereas other members of the analogous series (monomesogenic, bimesogenic, cyclic and polymer) are seen to form only S_A phases. Excellent planar alignment was obtained using rubbed polyimide. Dielectric reorientation occurred at voltages equivalent to those required for 5CB at the same reduced temperature, and a high contrast ratio between the switched and non-switched states was observed in the TN cell geometry. These effects could be stored on cooling below Tg and offer interesting possibilities for polarisation rotating (or not) optical elements. Similarly inclusion of ferroelectric NLO moieties[13] opens up a new range of $\chi 2$ and $\chi 3$ materials. The thermal behaviour and electro-optic properties of the smectic exhibiting homologues in the cyclic series will be presented at a later date, along with further analysis of this nematic compound.

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