Physical Properties of Siloxane Containing Oxycyanobiphenyl Derivatives for Smectic-A Device Applications

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In this paper we report on a homologous series of oxycyanobiphenyl liquid crystals with pentamethyldisiloxane units substituted onto the end of the alkoxy chain. We present fast switching times in the order of milliseconds, threshold voltages of ∼2 V/μm, and show that these properties are relatively temperature independent. Measurements were made by means of electro-optical microscopy. Experiments were conducted in both the high frequency (dielectric) mode and also in the low frequency (scattering) mode. We find that the measured properties are dependent upon the length of the alkoxy chain and that the longer spacer chains, n ≥ 8, give low threshold voltages, fast response times and a distinct high frequency-low frequency crossover mode.

Keywords: display; optical storage; scattering; smectic A

INTRODUCTION

The Smectic A (SmA) scattering device, first reported in 1978 [1], operates in two distinct regimes, which are stable and are optically clear and scattering, respectively. The cyanobiphenyl based liquid crystals, Figure 1, presented here with a siloxane moiety substituted to the end of the alkoxy chain, have positive dielectric anisotropy, with a negative conductivity anisotropy due to the SmA phase. These organosiloxane materials do not, in general, develop a nematic phase.

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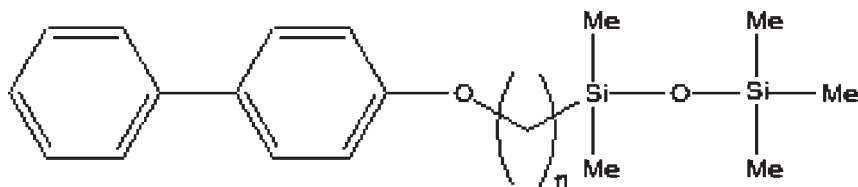
FIGURE 1 Schematic diagram of the homologous series of organsiloxane-oxycyanobiphenyl liquid crystals, based on the 4-(ω-alkenyloxy)-4′-cyanobiphenyl mesogenic unit with pentamethyldisiloxane tail, where n is the number of carbon atoms in the alkyl chain.

Application of a high frequency (HF) alternating voltage, across the sample, results in reinforcing the homotropic texture by dielectric reorientation [2]. Application of a zero or low frequency (LF) electric field results in motion of ionic impurities, in a plane perpendicular to the applied electric field (within the smectic layers), and leads to electro-hydrodynamic instabilities (EHDI); the resulting turbulent motion causes light scattering by the formation of curvature deformations in the SmA layers. The impurities are generally introduced by doping with a very small quantity of ionic molecules; which has implications with regard to filling of the display [3]. Curvature in the SmA layers is a relatively low energy splay elastic deformation and the scattering and clear states, therefore, do not tend to relax. In this way, the device promises polarizer free switching, with stable switch states. The threshold field for switching is a function of the surface feature height and this caused problems for early device fabrication; a study of the surface topology is presented in [1]. It is found that turbulent motion initiates from a defect in the texture, at the electrode edge or other site of curvature in the SmA layers. For this reason a period of "burn in" of the device is often necessary, where microscopic pitting of the substrate surface occurs, so that curvature exists in the clear state, ready for a switch to the scattering state.

THEORY

We define our model of a SmA liquid crystal, shown in Figure 2, as having homotropic alignment, with smectic layers parallel to the two containing glass substrates. The relevant parameters in context of the SmA scattering display are the layer curvature, $\Psi = d\theta/dx$, and the charge, q. The dynamics of these quantities may be modelled by
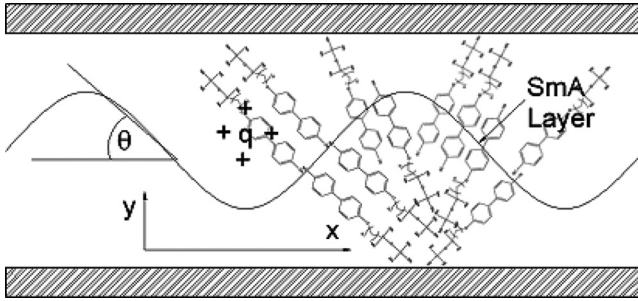
FIGURE 2 Schematic diagram of the SmA scattering display. The charge is q and the curvature $\Psi = d\theta/dx$. During switching an electric field is applied along the y-axis.

Navier–Stokes equations [4]:

$$\frac{d\Psi}{dt} + \frac{\Psi}{T} + \frac{qE}{\eta} = 0 \tag{1}$$

$$\frac{dq}{dt} + \frac{q}{\tau} + \sigma_H E\Psi = 0 \tag{2}$$

E is the electric field, T is the relaxation rate for the curvature, τ is the relaxation rate for charge, and η is the effective viscosity:

$$
\begin{aligned}
\frac{1}{T} &= \left(\frac{4}{\mu}\right)\left(\frac{\varepsilon_\parallel}{\varepsilon_\perp}\frac{\Delta\varepsilon}{4\pi}E^2 + K_{11}k^2\right), \\
\frac{1}{\tau} &= \frac{4\pi\sigma_\perp}{\varepsilon_\perp}, \\
\frac{1}{\eta} &= \frac{4}{\mu}\frac{\varepsilon_\parallel}{\varepsilon_\perp}, \\
\sigma_H &= \sigma_\perp\left(\frac{\varepsilon_\parallel}{\varepsilon_\perp} - \frac{\sigma_\parallel}{\sigma_\perp}\right)
\end{aligned}
\tag{3}
$$

μ is a viscosity coefficient, K_{11} is the splay elastic constant, k is the wave vector of the curvature, σ is the conductivity and ε is the dielectric constant. Solving these equations leads to the observation that the charge is independent of time at high frequencies and the curvature is independent of time at low frequencies and this leads to the presence of the high and low frequency regimes.

J. R. Willmott et al.

The threshold voltage, V_{th}, is given by [5]:

$$V_{th}^2(LF) = \frac{2\pi k_{11}d}{\varepsilon_0\varepsilon_\parallel\left(-\dfrac{\Delta\sigma}{\sigma_\perp}\right)\lambda} \qquad (4)$$

$$V_{th}^2(HF) = \frac{2\pi k_{11}d}{\varepsilon_0\Delta\varepsilon\lambda} \qquad (5)$$

The measured response time for SmA switching is dependent upon the speed at which the scattering texture spreads from seed sites and is given by [6]:

$$\nu\left(\mu m \cdot s^{-1}\right) = \left(1.8 - \frac{T_{SmA\to N}}{T}\right)(V - V_{th}) \qquad (6)$$

where $T_{SmA\to N}$ is the SmA to nematic phase transition and T is the sample temperature.

EXPERIMENTAL

A homologous series of organosiloxane liquid crystals was synthesised [7] and this is shown schematically in Figure 1. Thermo-optic transition temperatures are presented in Table 1, as a function of alkyl chain length. A small quantity (0.01%) of ionic impurity, Cetyltri-methylannonium Bromide or CTAB (Sigma-Aldrich), was mixed with the samples. Pure materials were characterised by optical microscopy, DSC and X-Ray studies and each were found to possess a single SmA mesophase [9]. Electro-optic measurements, of ionically doped samples, were by means of an Olympus BH2 polarising microscope,

TABLE 1 Transition Temperatures of the Homologous Series of Liquid Crystals that were Studied, Together with X-Ray Data and with Molecular Lengths; Measured by Molecular Simulation (Software from Tripos).

n	Phase	d (Å)	L (Å)	d/L
4	K 39.1 S [28.7] 1	34.4	21.3	1.615023
5	K 30.4 S 50.3 (2.2) I	36.4	22.6	1.610619
6	K 36 S 53.8 (5.1) I	39.4	23.8	1.655462
8	K 37 S 60.9 (4.1) I	42.6	26.2	1.625954
10	K 37.9 K′ 41 S 68 (3) I	49.6	28.7	1.728223
11	K 30 S 73 (3) I	51	30	1.7

The smectic layer thickness is d, n is the number of carbon atoms in the alkyl chain and L is the molecular length.

in combination with a photodiode and detection electronics. Sample temperature was controlled by a hot stage, manufactured by Linkam Ltd. Cells were constructed from glass substrates coated with conductive ITO, rubbed polyimide, spaced by 14 μm and were obtained commercially from EEV. The experimental apparatus has been further described in a previous publication [8].

Measurements were made of the threshold field and response time of the different materials as a function of temperature. Following [1] we define the threshold field differently from that in the theory section, due to the way in which it is measured, which will be the same except for a constant factor. The measured V_{th} is the electric field at which the transmission of the cell is midway (50%) between the transmission of the clear state and that of the scattering state, rather than the onset which is functionally the same. The critical frequency is defined as the frequency at which the electro-optic characteristics of the sample change from the clear state to the scattering state, as the frequency of an applied AC field is slowly decreased. This marks the boundary between the HF and LF regimes.

RESULTS

Threshold field and response time measurements were made in order to elucidate structure property relationships and to characterise these siloxane-cyanobiphenyls for device applications.

The temperature dependence of V_{th} is shown in Figure 3. The trend, for both HF and LF regimes is relatively temperature independent, except at the clearing point where V_{th} is seen to decrease rapidly. This correlates with X-ray scattering data, Table 1, where the inter layer spacing is independent of temperature away from the clearing point. By definition, the order parameter in the smectic phase is related to the layer spacing and is, therefore, temperature independent; following Eqs. (7) and (8), if the dielectric anisotropy and splay elastic constant do not change then the threshold voltage will be temperature independent.

The response time as a function of temperature is shown in Figure 4. Fast response times are likely to correlate with low elastic constants and high dielectric anisotropy. We find that the response time increases as the temperature decreases, though it is once again relatively temperature independent away from the clearing temperature, with only a slow upward drift; for similar reasons given to explain the threshold field temperature dependence. It is likely that the high order and molecular associations at low temperature inhibits the motion of the dopants, which is consistent with the observed trend
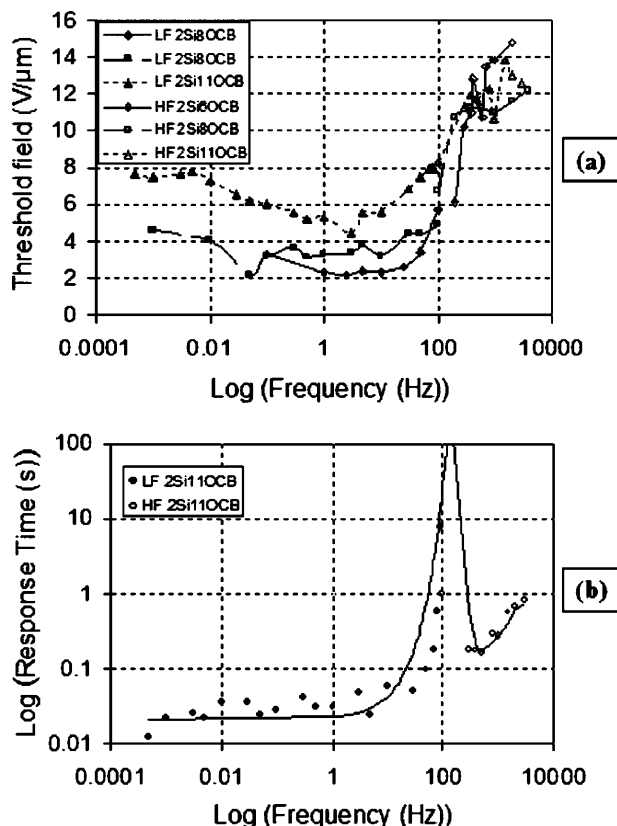
FIGURE 3 (a) Temperature dependence of the threshold field for HF (1 kHz) switching and (b) LF (1 Hz) switching.

at low frequency switching. The faster HF switch at higher temperatures is most likely due to the lowered viscosity of the material near the clearing point. It is interesting to note that materials with n = 5, 6 switch significantly more slowly that the other homologues. Comparison of the n = 8 material shows that this material is both fast switching and exhibits a low threshold field for switching, which is clearly an important observation for device applications. The frequency dependence of the threshold voltage and response time is presented in Figure 5. We find a pronounced critical frequency, at approximately 100 Hz, between HF and LF switching regimes. Therefore, only a simple drive scheme, involving frequency doubling the addressing voltage, would be required for a SmA scattering display
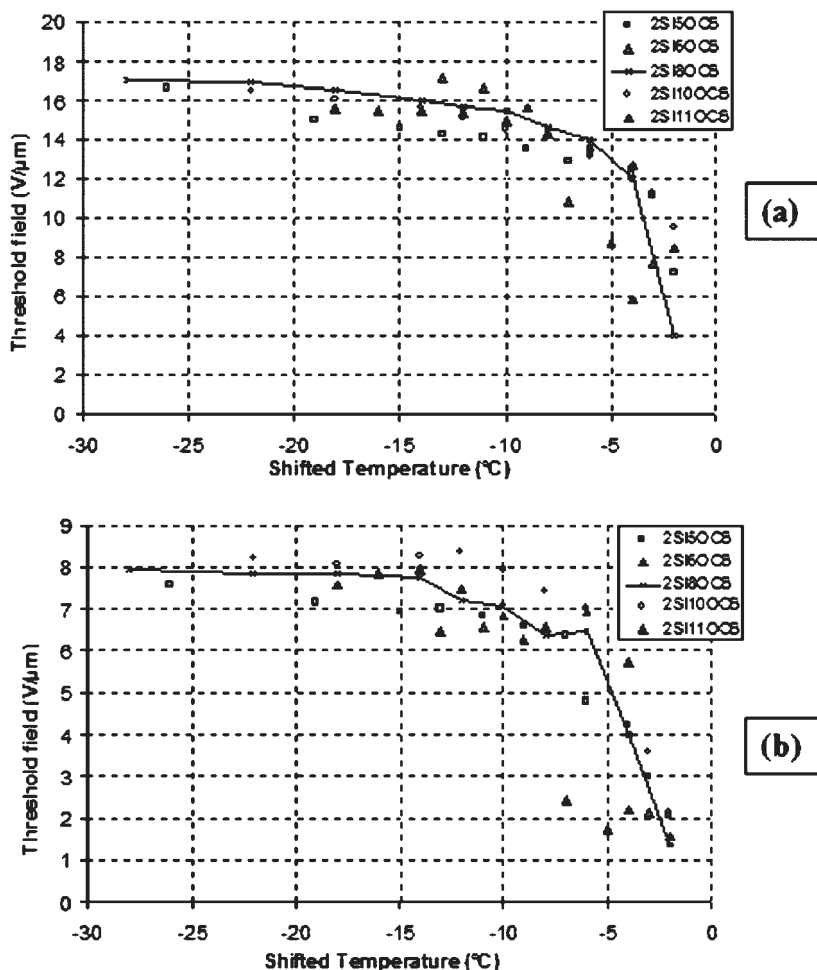
FIGURE 4 (a) Temperature dependence of the response time for HF switching (applied field E = 9.1 V/μm) and (b) LF switching (E = 5.7 V/μm).

incorporating these materials. Broadly, the switching of these siloxane liquid crystals is a factor of ten faster than the equivalent materials without siloxane [1].

CONCLUSIONS

Given the results for the threshold field and response time of a homologous series of organosiloxane-oxycyanobiphenyl liquid crystals,
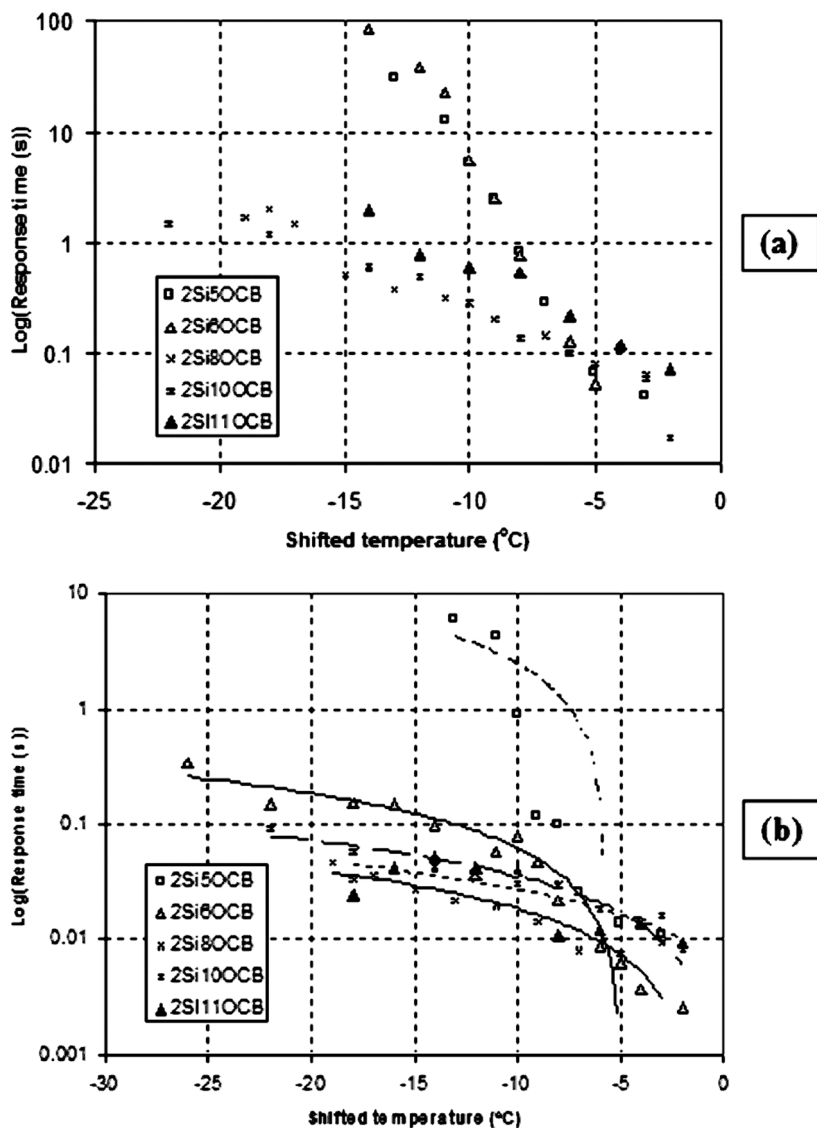
FIGURE 5 (a) Frequency dependence of the threshold field and (b) response time. The filled data points refer to the LF regime and the unfilled data refer to the HF regime.

in the SmA scattering display mode, it would seem that siloxane containing liquid crystals are very promising for SmA display applications. These materials exhibit a SmA phase over the entirety of their

wide mesophase and away from the clearing temperature they are notable for their relative temperature independent properties. The millisecond response times of these materials is a factor of ten faster than the response times of equivalent materials without siloxane, which is in the order of seconds for HF switching and 100 milliseconds for LF switching. The material with eight carbon atoms in the alkyl chain exhibits both low threshold voltage and fast response time.

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