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Electroclinic behaviour of polymer doped low molar mass ferroelectric liquid crystals

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Recently there has been much interest in the electroclinic effect due to its potential application in high speed optical modulators and grey scale displays. In present materials, however, the electroclinic effect is very dependent on temperature and falls off rapidly with increasing temperature. This limits the useful device operating range. In this paper the electroclinic behaviour of new, side chain polymer doped, low molar mass ferroelectic liquid crystal mixtures is reported. By measuring the rate of change of the electroclinic coefficient with temperature it is shown that the temperature range over which the electroclinic effect exists increases with polymer concentration. Data are also presented on electroclinic response times.

1. Introduction

The electroclinic effect in a S_A material consisting of chiral molecules was first reported by Garoff and Meyer [1]. When an electric field is applied normal to the director an induced field-dependent tilt is observed. Since the electroclinic effect is not a bistable phenomenon and any induced electroclinic tilt may be uniquely specified by an applied field, the electroclinic effect is well suited to applications in optical modulation and grey scaling. Under low fields and at temperatures not too close to the S_C^*–S_A phase transition, the induced tilt θ is linear in electric field [2]. With high electric fields or low temperatures, which give rise to tilt angles greater than a few degrees, the response becomes non-linear and follows a $\theta \propto E^{1/3}$ law [2].

Response times associated with electroclinic switching are generally much shorter than ferroelectric responses. The electroclinic response is governed by the viscosity relating to the inclination of the molecules, the tilt controlling susceptibility [1] and also the applied voltage and cell thickness [2, 3]. Modulation above 1 MHz is easily achievable in current low molar mass materials. The optical quality of an electroclinic cell is generally much higher than that of a S_C^* phase ferroelectric cell since the layer shrinkage associated with the S_A–S_C^* phase transition does not occur in the S_A phase. Few of the defects commonly found in S_C^* phase ferroelectric devices are present in a well aligned smectic A device. However, the electroclinic effect is very dependent on temperature and tilt angles large enough for use in devices exist over only a few degrees around the S_C^*–S_A phase transition. Also, induced electroclinic tilt angles greater than 10° are difficult to achieve and require high fields ($> 20\,V\,\mu m^{-1}$) which many degrade the liquid crystal and increase the defect content of the texture. In order to gain maximum contrast in a birefringence device a tilt of 22·5° is required. Any current, commercial device would, therefore, require costly temperature stabilization and would not operate at maximum possible contrast.

This paper describes an enhancement of the electroclinic characteristics of the commercial ferroelectric material SCE 13 (Merck Ltd, UK) on addition of a

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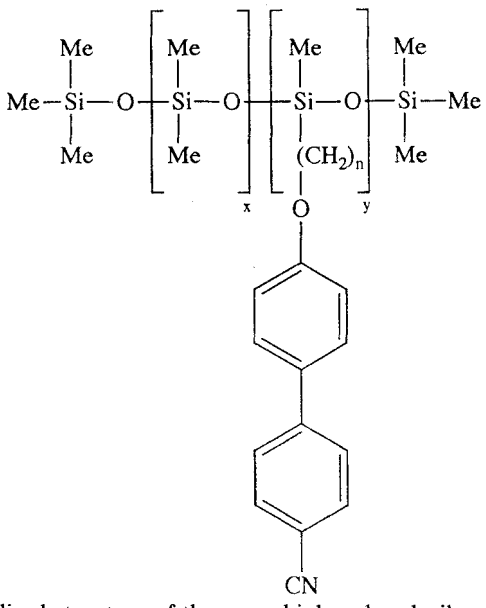


Figure 1. The generalized structure of the cyanobiphenyl, polysiloxane, smectic A polymer.

cyanobiphenyl side chain, polysiloxane polymer, see figure 1. The results for three concentrations are presented here.

2. Experimental

The polymer/SCE 13 mixtures were made in concentrations of 0 per cent, 1·3 per cent and 2·4 per cent w/w. The mixtures were shaken for several hours at 130°C. This ensured that good mixing was achieved. 2 μm planar cells, with anti-parallel rubbed polyimide alignment layers were then vacuum filled with the mixtures and slowly cooled from 110°C to the S_A phase. Very good alignment was observed and the cells were effectively defect free. Temperature was controlled by a Mettler hot stage and controller (FP 80 and FP 82) accurate to 0·1°C and samples were observed using an Olympus BH 2 polarizing microscope with photodiode attachment.

The technique used to measure the electroclinic tilt angles is based on a method described by Qui, Ho and Hark [4]. It relies on detecting the changes in intensity transmitted through the electroclinic cell as it switches through different induced tilt angles. A cell placed between crossed polarizers, with no applied electric field will transmit an intensity

$$I = I_0 \sin^2(2\alpha) \sin^2\left(\frac{\pi d \Delta n}{\lambda}\right), \tag{1}$$

where I_0 is the intensity of incident light, α is the angle of the director to the first polarizer, d is the sample thickness, Δn is the birefringence of the sample and λ is the wavelength of the incident light. When an electric field is applied across the cell a field dependent tilt angle will be induced. By differentiating equation (1), the change in intensity, δI, corresponding to a small induced tilt angle, θ, is given by

$$\delta I = 2I_0 \sin(4\alpha) \sin^2\left(\frac{\pi d \Delta n}{\lambda}\right)\theta. \tag{2}$$

By orienting the cell such that the director is at 22·5° to the first polarizer ($\alpha = 22{\cdot}5°$), the change in intensity, δI, is maximized. The induced tilt angle is then given by

$$\theta = \frac{\delta I}{4I}, \tag{3}$$

where I is the intensity transmitted through the unperturbed cell.

A 100 Hz bipolar triangular waveform, generated by a Thurlby–Thandar TG 1304 function generator, was applied to the sample. The transmitted intensity was detected by a fast photodiode mounted in the microscope, amplified by an in-house amplifier and the output voltage was measured using a Hewlett–Packard HP 54502a digitizing oscilloscope. The change in transmitted intensity, δI, was taken to be proportional to half the peak–peak value of the output voltage and the unperturbed transmitted intensity, I, was taken to be proportional to the average value of the output voltage. The hot stage, function generator and oscilloscope were all interfaced to a Viglen 386 personal computer which allowed the temperature and the field across the sample to be varied automatically and the value of the corresponding tilt angle to be logged.

3. Results

The phase sequences of the low molar mass host, the polymer and the mixtures were determined by optical microscopy. The values measured are shown in the table. In this paper the S_C^*–S_A phase transition temperature will be denoted by T_C.

The tilt angles for each of the three samples were measured against temperature and applied voltage. The temperature was varied from just below T_C to at least 8°C into the S_A phase and voltage was varied from 0·1 V to 2·0 V in steps of 0·1 V. Using such low voltages ensured that any non-linearities in the dependence of tilt angle on voltage were due only to the critical behaviour close to T_C rather than non-linear behaviour with E. A plot is shown in figure 2 to exemplify the linearity of the data and the resolution of the experiment, which was estimated to be better than 0·005°.

The plots of tilt angle versus temperature for SCE 13 and the mixtures are shown in figure 3 for two different applied voltages. It can be seen that, for a given reduced temperature ($T - T_C$), the electroclinic tilt angle increases with polymer concentration. A fuller picture is provided by plotting the electroclinic coefficient, $E(T)$, for each material against temperature. In this paper the electroclinic coefficient has been taken as the rate of change of induced tilt angle with applied r.m.s. voltage, V, across the cell.

$$E(T) = \frac{d\theta}{dV}. \tag{4}$$

To calculate the electroclinic coefficient at each temperature, the tilt angle θ, versus applied voltage, V, data were fitted to straight lines. The plots of electroclinic coefficient

Phase transition temperatures of the samples used. The solid to smectic transition temperatures were not measured for two mixtures.

Sample	Phase transition temperature/°C								
Polymer	Glass	−10	S_A	56	S_A/I	120	Isotropic		
SCE 13	Solid	−20	S_C^*	60·8	S_A	86·3	N*	100·8	I
1·3 per cent polymer			S_C^*	48·0	S_A	89·8	N*	104·0	I
2·4 per cent polymer			S_C^*	27·5	S_A	94·7	N*	105·0	I

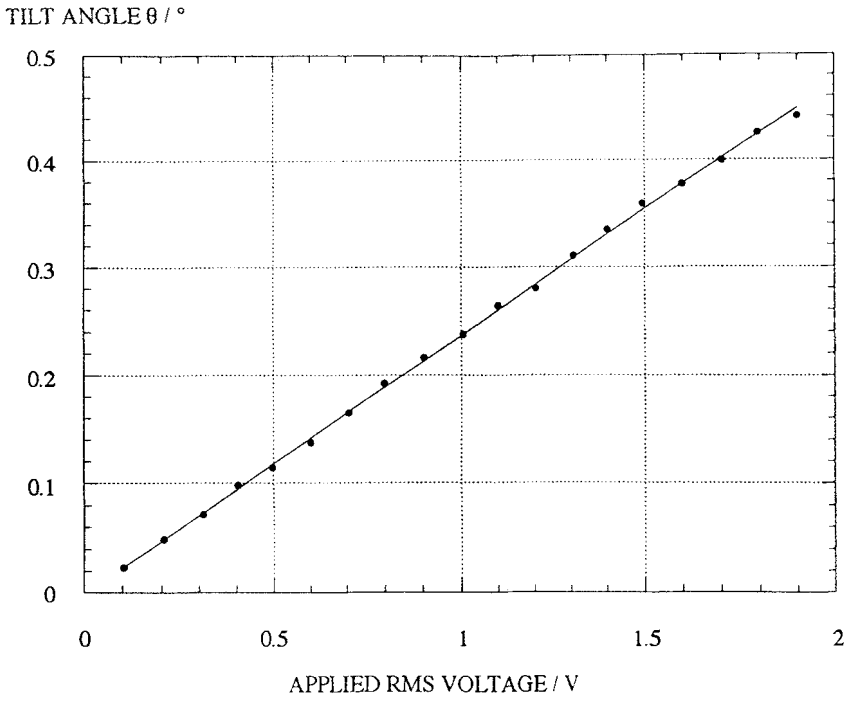


Figure 2. A typical plot of tilt angle (θ) versus applied voltage (V) at constant temperature. The resolution of the experiment was estimated to be 0·005°. The size of the points represents the size of the error.

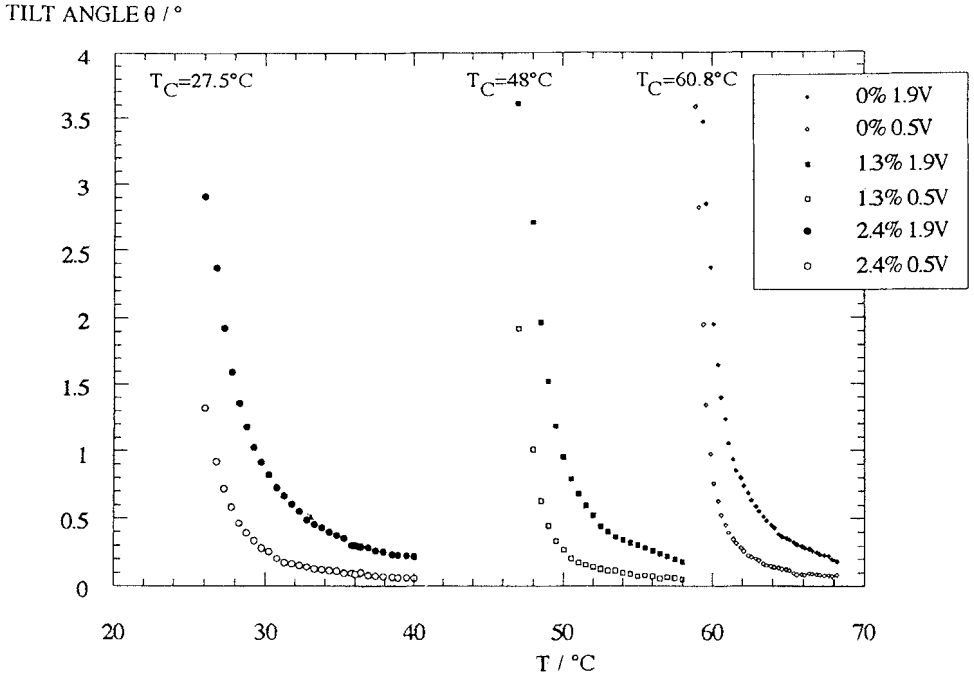


Figure 3. A plot of tilt angle versus temperature for SCE 13 and the mixtures. The voltage was varied from 0·1 V to 1·9 V, but only the plots for 0·5 V and 1·9 V are shown to aid clarity.

versus temperature for SCE 13 and the mixtures are shown in figure 4. Besides the depression of the ferroelectric phases to lower temperatures, the most noticeable feature of the graph is the increased range over which the electroclinic effect exits for mixtures with higher polymer concentrations.

According to electroclinic theory [2, 5], away from the S_C^*–S_A phase transition, the electroclinic coefficient, $E(T)$, is proportional to $1/(T - T_C)$. By plotting $1/E(T)$ versus temperature T, we were able to compare our data with the theoretical model. The graphs of $1/E(T)$ versus temperature for SCE 13 and the mixtures are shown in figure 5. It is clear from the graphs that away from the S_C^*–S_A phase transition, $1/E(T)$ is linear in $(T - T_C)$ and close to the transition, $1/E(T)$ becomes non-linear in $(T - T_C)$. Interestingly, the temperature range of the non-linear region increases with increasing polymer concentration, suggesting that the S_C^*–S_A phase transition is becoming broader or that pretransitional ferroelectric switching is influencing the electroclinic coefficient, $E(T)$.

4. Response times

A 100 Hz square wave was applied to the sample cells and the optical response monitored on the oscilliscope. The response times were taken as the 10–90 per cent times of the rising edge. The measurements were made over a reduced temperature range of $0°C \leqslant (T - T_C) \leqslant 8°C$ and a peak–peak voltage range of $0\,V \leqslant V_{PP} \leqslant 2{\cdot}5\,V$. The results are shown in figure 6 (*a*)–(*c*). The response time plots show that away from the transition and at the low voltages used, the electroclinic response is more or less independent of applied voltage as predicted by electroclinic theory [2, 5]. At the phase transition, the response is more ferroelectric in nature, showing a strong voltage dependence. This correlates with the non-linearities in the 1/electroclinic coefficient

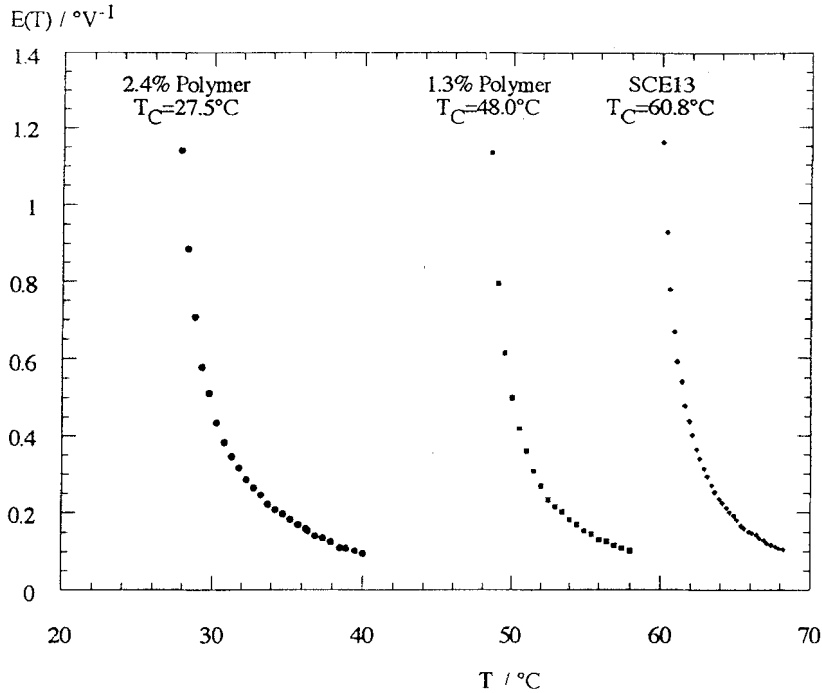


Figure 4. The electroclinic coefficient, $E(T)$, versus temperature for SCE 13 and the mixtures. T_C denotes the unperturbed S_C^*–S_A phase transition temperature.

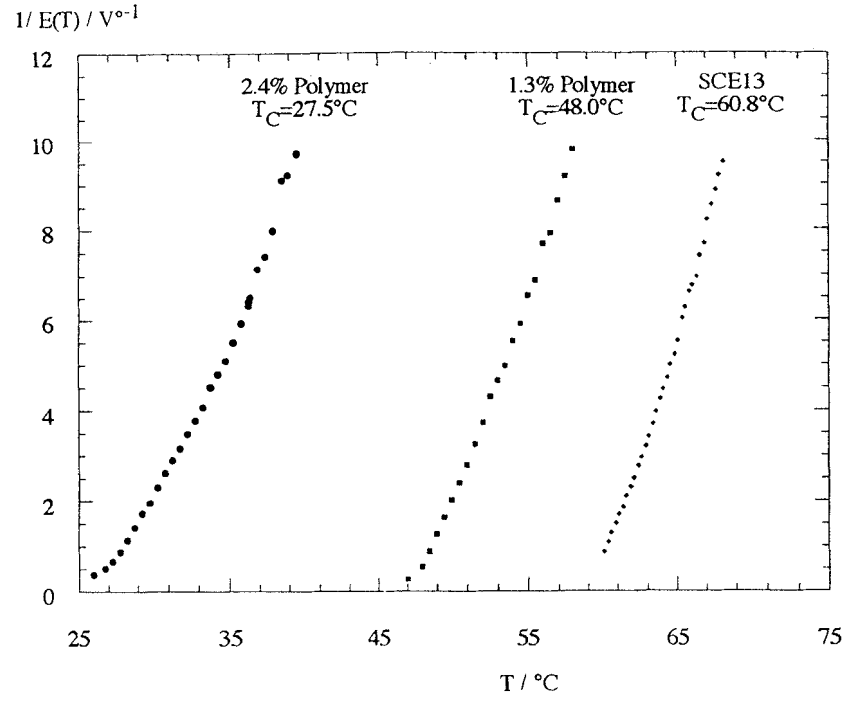
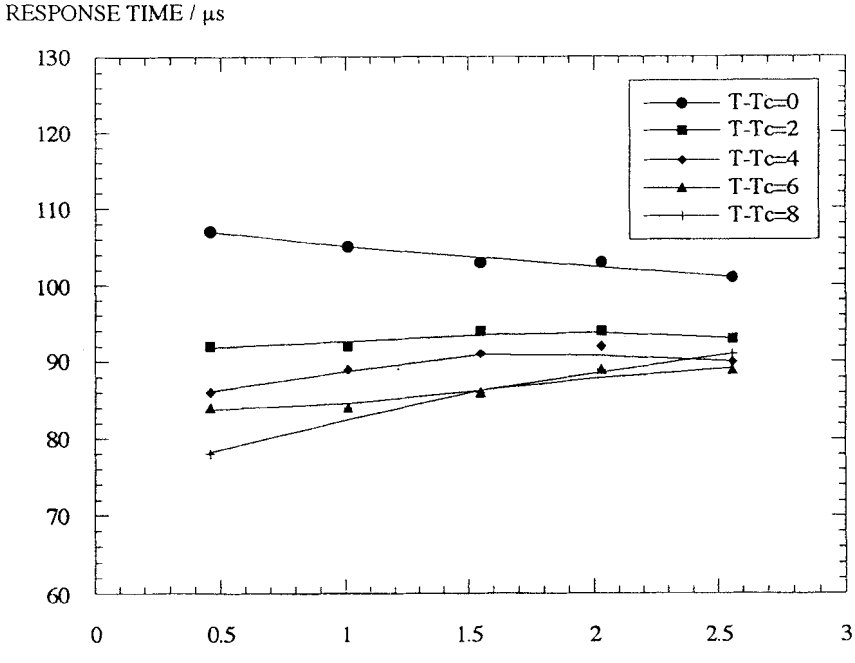


Figure 5. 1/electroclinic coefficient, $E(T)$ versus temperature for SCE 13 and the mixtures, T_C denotes the unperturbed S_C^*–S_A phase transition temperature.



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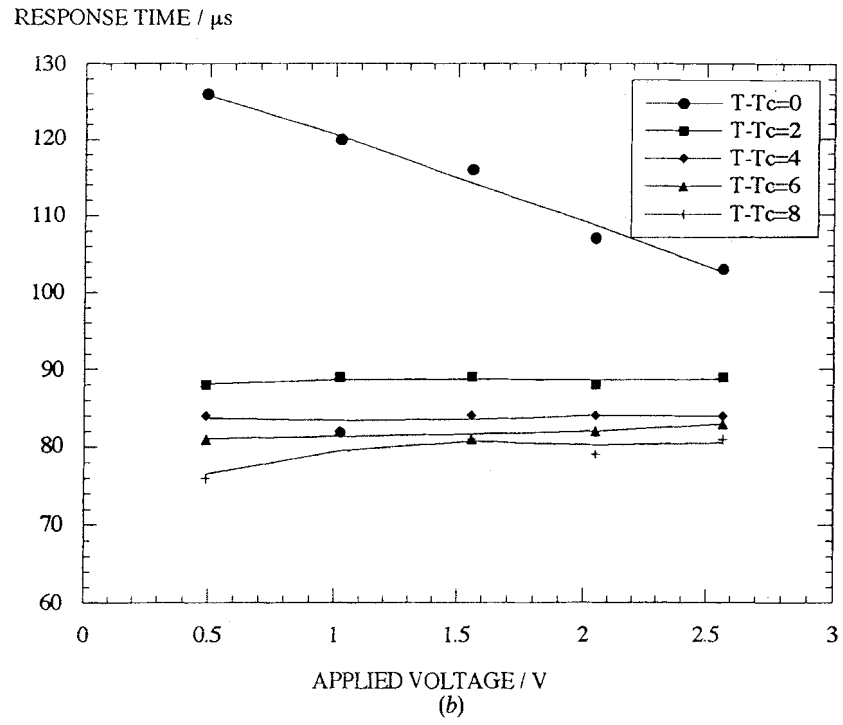

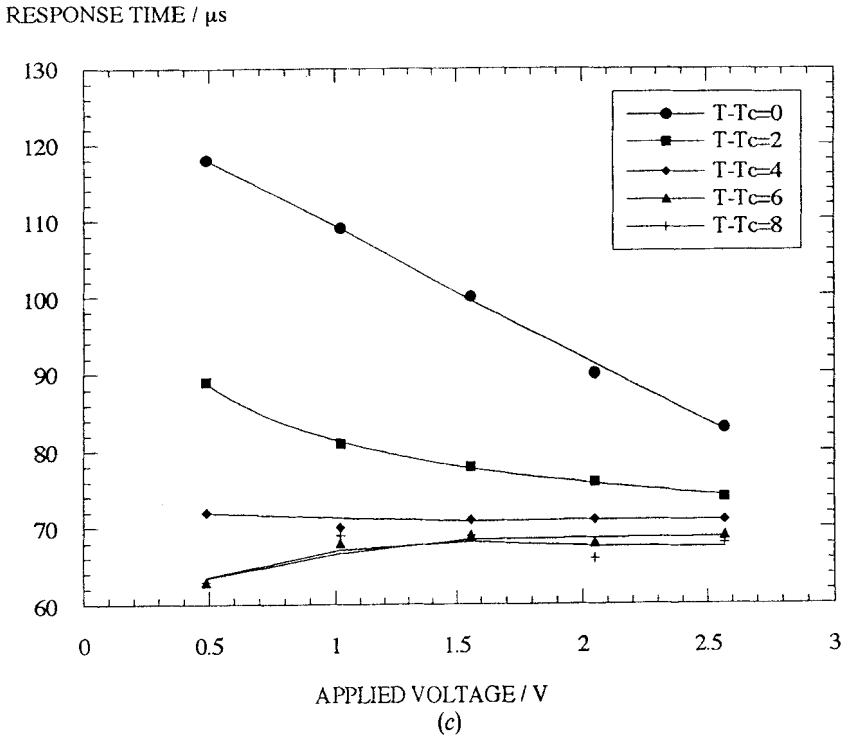

Figure 6. (*a*) Response time versus applied voltage for the pure host. (*b*) Response time versus applied voltage for the 1·3 per cent polymer mixture. (*c*) Response time versus applied voltage for the 2·4 per cent polymer mixture. The estimated error on the data was $\pm 3\,\mu s$.

versus temperature data. Interestingly, the response times away from the transition tend to decrease with increasing polymer concentration. This indicates that the molecules are able to be switched more easily and that there may be a lower rotational viscosity. Also, the ferroelectric nature of the response time extends further into the S_A phase for mixtures with a higher polymer concentration. This again suggests that the S_C^*–S_A phase transition is becoming broader.

5. Conclusion

The results of our preliminary studies show that on addition of a smectic A polymer to a low molar mass ferroelectric host we have observed three important features.

First, we have observed a rapid predomination of the S_A phase with increasing polymer concentration. The polymer has a strong smectic A nature which lowers the S_C^*–S_A transition temperature and raises the S_A–N^* transition temperature of the host ferroelectric liquid crystal.

Secondly, we have observed an increase in the electroclinic coefficient of the host ferroelectric liquid crystal on addition of the smectic A polymer. Consequently, the temperature range over which the electroclinic effect exists is increased. Also, the graphs of 1/electroclinic coefficient versus temperature and the response time measurements suggest that the S_C^*–S_A phase transition may be broadened on addition of the polymer.

Thirdly, we have observed a decrease in the electroclinic response time with increasing smectic A polymer concentration.

At this stage it is not clear exactly how the polymer is affecting the structure of the low molar mass host. However, we do believe that the polymer backbone lies parallel to the smectic layering and that it may be affecting the interlayer separation and interaction. In this situation the molecular mean field is altered and low molar mass molecules are able to be switched more easily as the layers become more decoupled.

Future work will involve X-ray studies and birefringence measurements to help determine the molecular conformation and structural model. This will reveal a much clearer picture of the role of the polymer. Differential scanning calorimetry will give some indication of any first order behaviour of the S_C^*–S_A transition induced by the polymer and measurements will be made at higher polymer concentrations and higher voltages. We will then be able to determine the role of the polymer in determining the critical dependence of the electroclinic coefficient on temperature.

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