polymer papers

Side chain polysiloxane liquid crystals and their behaviour in electric fields*

R. Simon and H. J. Coles†
Liquid Crystal Group, Physics Department, The University, Manchester, M13 9PL, UK
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Optical and electro-optical properties of side chain liquid crystalline polymers are described. The polymers studied were homopolysiloxanes with mesogenic side groups separated from the polymer backbone by flexible polymethylene spacers of varying length. The effect of the flexible spacer on the phase properties and electric field effects will be discussed. Low frequency a.c. fields induced a turbulent scattering texture, whilst at higher frequencies (> 1 kHz) a homeotropic alignment was obtained. The latter effect leads to high contrast displays which are durably stored at temperatures well above the glass transition. Various parameters affecting the response of the polymers to applied fields will also be discussed. These include temperature, frequency and magnitude of the electric field, film thickness and the length of the flexible spacer.

INTRODUCTION

During the early 1970's a wide range of commercially useful low molar mass liquid crystals were developed which found numerous applications in the visual display industry. Over the last few years the liquid crystal and polymer science fields have combined to produce polymers exhibiting thermotropic liquid crystalline behaviour. These include main chain[1], side chain[2] and crosslinked[3] polymers. Like low molecular weight liquid crystals, these polymers can show smectic, nematic and cholesteric mesophases. In an effort to discern whether these materials were of use in display devices, the behaviour of nematic and cholesteric polymers in electric fields has been investigated[4-7]. The conclusions drawn were that, although the threshold voltages for electro-optic effects were in some cases comparable to those in low molar mass liquid crystals, the slow response of the polymers to applied fields precluded them from use in active displays. On the other hand, it was found that the presence of a glass transition in the polymer enabled thermally and electric field induced liquid crystalline textures to be durably stored at temperatures below T_g. Thus, side chain polymeric liquid crystals, in particular, have found applications as storage materials. To be of practical use, however, materials with glass transition temperatures well above ambient are needed, in which case the temperatures needed to 'write' the textural information can be prohibitively high.

Recently, our investigations on smectic side chain polysiloxanes[8] have shown that successful storage of electrically written information does not need to be at temperatures below the glass transition, and textures can be readily stored in the liquid crystalline phase of such compounds. Such storage effects were the first to be reported in side chain polymeric liquid crystals.

Since in low molar mass liquid crystalline systems the length of the flexible alkyl chain has a marked effect on the

phase behaviour and subsequent electro-optic properties of such compounds, similar effects might be expected in polymer systems. In this paper, therefore, we report data on a series of side chain polysiloxanes[9] differing only in the length of the flexible spacer separating the liquid crystal moiety from the polymer backbone. These data will be discussed in terms of the observed optical and electro-optical properties.

EXPERIMENTAL

Materials

The polymers studied were two series of side chain homopolysiloxanes of general structure
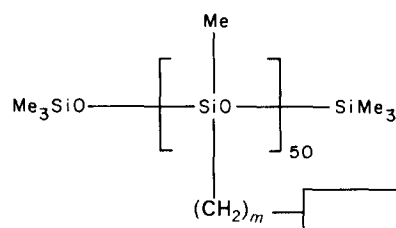
and differing only in the mesogenic unit

These polymers, and the d.s.c. data on their phase transitions, were kindly supplied to us by Professor G. W. Gray, FRS, Dr D. Lacey and Dr P. A. Gemmell of Hull University. The chemical structures of the two series, and their phase transitions as a function of *m* (the length of the flexible alkyl spacer) are given in *Figures 1a* and *1b*.

Techniques

Optical microscopy of the polymers was carried out using an Olympus BH-2 polarizing microscope equipped with a LIN-KAM TH 600 hot stage and controller, calibrated to better than $\pm 0.1°C$ and capable of providing heating rates in the range 0.1 to 99°C min^{-1}. Thermo-optic analysis, in which the transmission of the polymer when viewed through crossed polars is measured as a function of temperature, was carried out using a linear response photodiode in place of one of the microscope
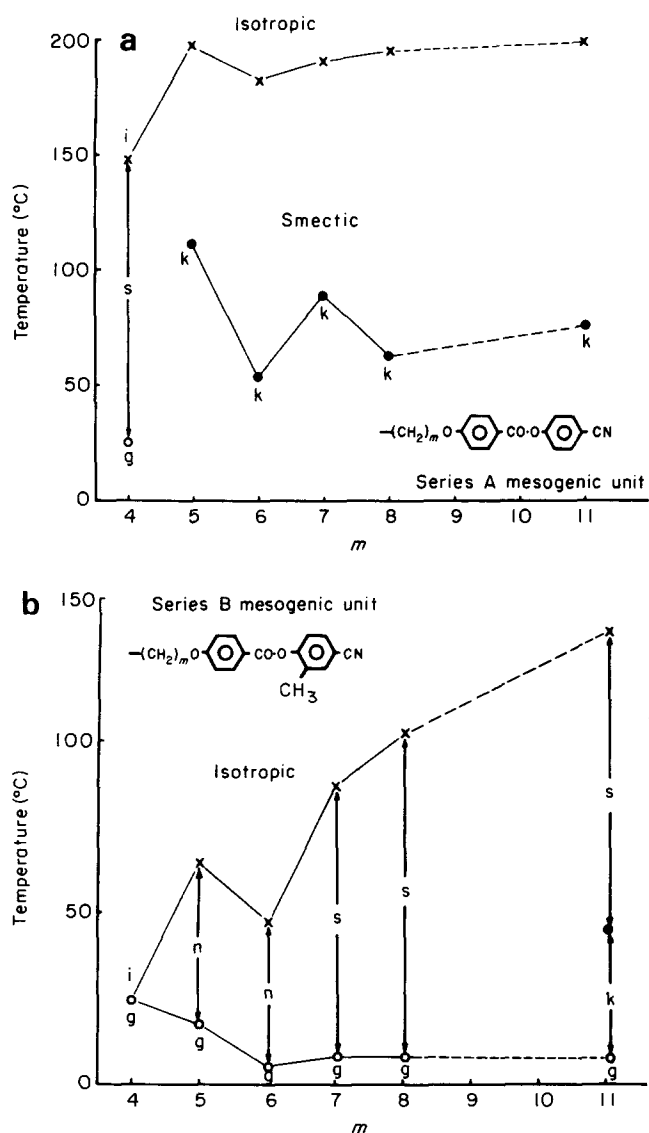
Figure 1 Phase transitions of (a) series A polymers, and (b) series B polymers, as a function of the number, *m*, of methylene units in the flexible spacer (n, nematic; s, smectic; k, crystalline; and i, isotropic phases)

eyepieces. The output from this photodiode was then plotted as a function of temperature using an *X–Y* recorder.

The polymers were studied by applying electric fields of varying voltage (0–300 Vrms), and frequency (d.c., 20 kHz), to thin (10–45 μm) samples sandwiched between two transparent conducting glass plates. Observations were again carried out using the optical microscope and the field was applied in the viewing direction.

RESULTS AND DISCUSSION

A number of features, evident from the transition data of *Figure 1*, indicate the effect of increasing the length of the flexible spacer. For both series A and series B polymers, an increase in the spacer length is accompanied by an increase in the liquid crystalline–isotropic phase transition. A tendency for the polymers to show a crystalline phase is also evident for the higher homologues. Both the liquid crystalline–isotropic and crystalline–liquid crystalline phase transitions show a marked odd–even effect, a feature which is also manifest in

low molar mass liquid crystals[10] and main chain polymeric liquid crystals[11]. An explanation proposed by Gemmell, Gray and Lacey[12] is that the polymers with odd spacer lengths (higher transitions) have the side chains at right angles to the regular backbone, while the even spacer polymers (lower transitions) have the side chains inclined to the backbone.

In polymers with a glass transition (series B), a gradual reduction in T_g is seen as the spacer length increases, leading to an increase in the range of stability of the mesophase. The stabilization of the smectic phases on increasing the spacer length, and the disruption of smectic behaviour by lateral substitution in the mesogenic moiety (compare series A polymers with the equivalent series B polymers), are well known in both the monomeric[13] and polymeric liquid crystalline fields and are seen to good effect in the polymers studied herein.

Thermo-optic analysis (TOA)

This technique measures the optical transmission, between crossed polars, of a thin polymer film as a function of temperature and, in conjunction with optical microscopy, is a useful tool in studying the characteristic properties of both nematic and smectic samples. *Figure 2* shows the TOA curves obtained from the smectic polymers A4 and A5 (where the letter denotes the polymer series and the number indicates the number of methylene units in the spacer) and the nematic polymer B5.

As is evident from the curves, the K–S, S–I and N–I transitions are all accompanied by a dramatic increase in the level of light transmission between crossed polars. The temperatures corresponding to the peak value of transmission for each transition agree to within 1 or 2 degrees with the d.s.c. values. All three samples exhibit a highly scattering texture at ambient temperatures which provides a low transmission between crossed polars.

On heating the nematic sample, B5, to a temperature some 5°C–10°C below the N–I transition temperature (using T_{NI} from d.s.c.), the transmission suddenly increases due to the appearance of a highly birefringent, coloured texture. Further increases in temperature cause the sample to run through a series of interference colours in accordance with the polymer birefringence reducing to zero. This results in the measured light transmission showing a maximum and decreasing to zero (i.e. the isotropic state, which shows extinction between crossed polars). A similar effect is seen in low molecular mass nematics, although the temperature range over which this happens can be as low as 0.1°C.

The curve for A5 has a similar shape to that of B5, but in this instance the reduction in transmission after the peak
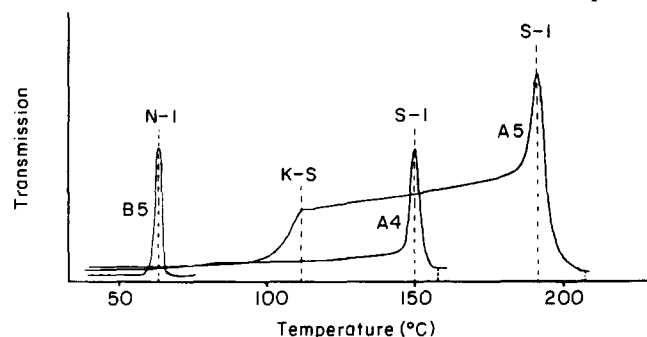

Figure 2 Thermo-optic analyses of three polymers, B5, A4 and A5. N–I, nematic to isotropic; K–S, crystalline to smectic; and S–I, smectic to isotropic phase transitions

value is caused by the appearance of the isotropic phase within the sample. Thus, it is possible to define two temperatures, T_{SI} and T_C, at which the isotropic phase first appears and where the last trace of birefringent texture disappears, respectively. At temperatures between T_{SI} and T_C the isotropic and smectic phases coexist in a stable biphasic region, and this property is common to all of the smectic polymers studied.

The optical textures of both the nematic and smectic polymers (i.e. B5 and A4, see *Figure 3c,d*), at temperatures close to the liquid crystalline–isotropic transition, were quite different to those observed for low molar mass nematic and smectic materials (see *Figure 3a,b*). No trace of a typical threaded texture was seen even on annealing the nematic polymer close to T_{NI} for long periods (days), and in the case of the sample A4, a typical smectic fan

texture was only observed after some 12 h annealing close to T_{SI}. Sample A5, however, exhibited a smectic fan texture on heating up to the smectic–isotropic transition (*Figure 3e*). The ease with which A5 exhibited a conventional smectic fan texture, and the need for extensive annealing of A4 to give a similar texture, suggests that the viscosity of the polymers at temperatures close to their liquid crystalline-isotropic transition differed somewhat, A5 being the more fluid polymer. In general, those polymers with high ($> 150°C$) liquid crystalline–isotropic transitions (i.e. A5–A11) were fluid enough to show a smectic fan texture on heating up to the transition, while those with transitions below this (B5–B11, A4) were more viscous and lengthy annealing treatments were necessary before characteristic textures were observed. Indeed, the shape of the TOA curves can be explained if one assumes
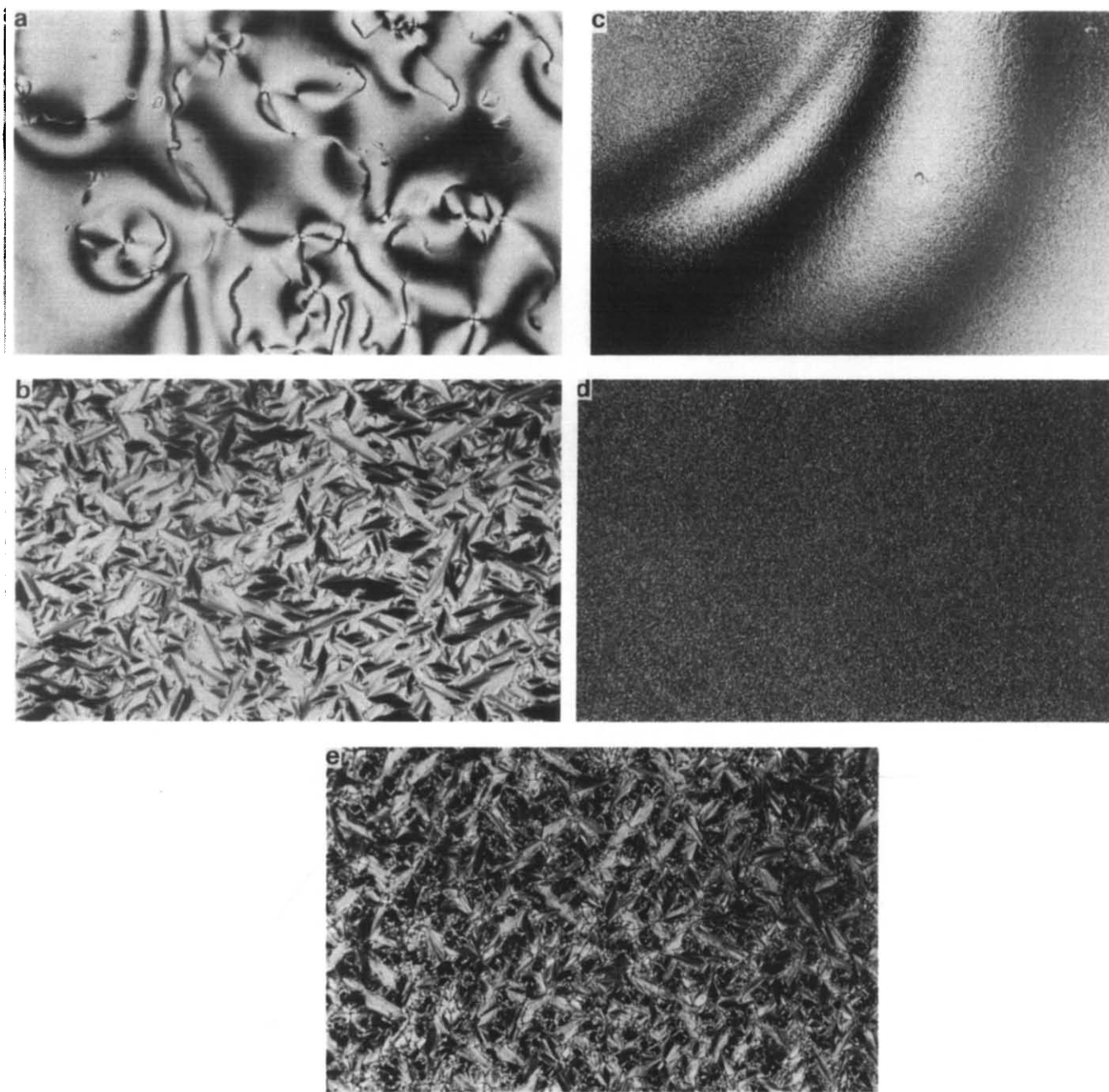

Figure 3 Photomicrographs exhibiting (a) a typical low molecular mass nematic threaded texture, (b) a low molecular mass smectic fan texture, (c) nematic texture shown by polymer B5, (d) smectic texture of polymer A4 and (e) the smectic texture of polymer A5. All photomicrographs taken between crossed polars, original magnification × 100

that a change in viscosity of the polymers occurs at a temperature just below the liquid crystalline–isotropic transition, allowing the mesogenic segments of the polymer freedom to acquire an anisotropic alignment, and hence appear highly birefringent between crossed polars.

Electric field effects

Electric field effects in smectic polymer liquid crystals with the cyanobiphenyl mesogenic moiety have recently been reported by us in the literature[8,14]. These effects were also seen in the two series of polymers under investigation and will be discussed in terms of the flexible spacer length, and the experimental variables, i.e. temperature, magnitude and frequency of the applied voltage, and the cell thickness.

For all of the polymers studied (with the exception of B4 which does not exhibit a liquid crystalline phase), the application of a d.c. electric field, above some threshold value, generated a turbulent motion within the cells. This turbulence was manifest at temperatures within 10°C–15°C of the liquid crystal–isotropic phase transition (T_{SI} or T_{NI}), and resulted in an increased intensity of scattered light which thus caused a decrease in transmitted light when the samples were viewed in the optical microscope. An example of the d.c. induced turbulence is seen to good effect in the photomicrographs of *Figure 4*. Prior to the application of the electric field, the polymer A8 exhibited a well defined smectic fan texture (*Figure 4a*) which was transformed to the highly scattering texture shown in the right hand side of *Figure 4b* after having been subjected to a 50 V d.c. field for some 5 s.
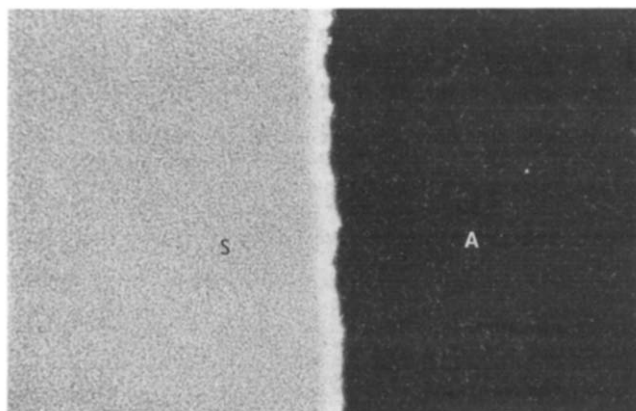
Figure 5   Induced textural change (dark area A) upon the application of a 60 Vrms, 2.5 kHz a.c. electric field across polymer A4 at 148°C in contrast to the scattering texture S. Crossed polars, original magnification × 100

The threshold voltage for the onset of turbulence varied from one polymer sample to another, being some 100 volts for the nematic polymers B5 and B6, falling to 60 volts for the smectic polymer B11, and further decreasing from around 56 volts for polymer A4 to between 20 and 25 volts for the higher homologues of the A series polymers. The voltage threshold was defined as the voltage which would induce a 10% drop in transmitted light intensity through the polymer film after application of the electric field for 5 min. The above data were obtained using a standard cell thickness of 25 ± 1 μm and at equivalent temperatures for the various polymers (i.e. 3°C below the T_{NI} or T_{SI} transition temperatures).

The speed of response of the polymers, to d.c. electric fields, was also studied, by applying voltages of twice the threshold value to the samples under the same condition of temperature and cell thickness as above. The time taken to saturate the drop in transmitted light intensity was found to vary from several minutes, for the nematic polymers B5 and B6, down to 2–3 s, for polymers A7–A11. This trend seemed generally to mimic the variation of threshold voltage.

Low frequency a.c. electric fields ($\leqslant 400$ Hz) also induced turbulent motion within all of the polymer samples, but on increasing the frequency of the applied electric field to above 500 Hz, the application of a voltage above threshold induced a realignment of the mesogenic side groups perpendicular to the cell walls, rather than a turbulence. This induced texture showed a high optical clarity which, on observation in the polarizing microscope, was uniformly dark between crossed polars. An example of this induced textural change is shown in the photomicrograph of *Figure 5*, for a 25 μm film of polymer A4 which had been subjected to a 100 Vrms, 2.5 kHz alternating voltage at 148°C for some 6 s. The contrast between the electric field aligned texture (A) and the scattering polymer texture (S) is also evident from *Figure 5*. Under the same conditions as were defined for the measurements of d.c. voltage thresholds (i.e. a 10% drop in intensity), a.c.$_{rms}$ voltage thresholds (at a frequency of 2.5 kHz), were measured for the two polymer series for this induced textural change. The same variation, from just over 100 V_{rms} for the nematic polymer B5, to around 20 V_{rms} for polymer A11, was found and similar trends were also observed for the response of the samples to voltages of twice the threshold value.
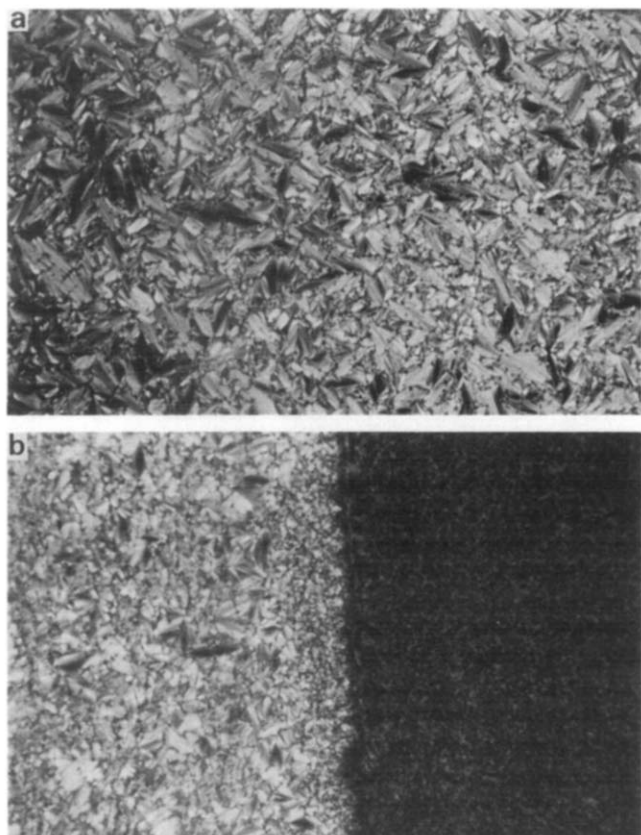

Figure 4   (a) Well defined smectic fan texture of polymer A8 and (b) textural change caused upon the application of 50 V d.c. across the right hand side of the sample. Crossed polars, original magnification × 100

The effects of varying the sample temperature, frequency and magnitude of the applied electric field, and sample thickness, on the response time for the induced transmission changes, were studied for all polymer samples. Certain general trends were observed which are outlined by the results presented below for the a.c. induced textural change in polymer A4. In these results, the rise time, τ_r, was defined as the time taken for the light transmission of the sample, between crossed polars, to fall to 50% of its initial value, and was used as a standard measure of the response.

Figure 6a shows the effect of increasing the rms voltage across a 25 μm layer of polymer A4. The measured rise time fell sharply from 30 s at an applied voltage of 87 V_{rms}, to some several hundred milliseconds at 240 V_{rms}. The temperature variation of the response time at a fixed applied voltage and frequency, is shown in *Figure 6b*. Again, the response time fell sharply, as the temperature of the sample was increased from 144.3°C to 153.8°C (the observed T_{SI} being 152.2°C) from 4 min down to a few seconds. Thus, at any particular applied voltage, it was possible to define a temperature threshold below which electro-optic responses were extremely slow (i.e. a temperature at which the applied voltage effected only a 10% drop in light transmission over a period of 5 min). This was measured at 144°C for the conditions described in *Figure 6b*.

The frequency dependence of the rise time was characterized by the curve of *Figure 6c*, showing an optimum frequency of around 2 kHz at which the response time of the polymer was a minimum. Between 400 Hz and 2 kHz, the rise time fell slightly from 28 s to 26 s, whilst above 2 kHz, τ_r, increased sharply to some 46 s at 20 kHz. Below 400 Hz, of course, only a turbulent scattering texture was induced. Since the voltage threshold of the sample was itself defined in terms of a response time, then its frequency dependence can also be assumed to be of the form of *Figure 6c*.

The cell thickness had a marked effect on the optical rise times of the polymer, thinner cells showing a much faster response than thicker cells, and the data of *Table 1* give the thickness dependence of the threshold voltage.

Thus, decreasing the layer thickness still further to around 6 μm (a standard cell thickness for conventional liquid crystal displays) implies a threshold voltage of around 10 Vrms or less, and quite moderate voltages could then be used to obtain response times on the millisecond timescale.

Storage effects

Both the d.c. induced scattering texture and the a.c. induced optically transparent texture were stored in the liquid crystalline phase of all polymer samples. This was achieved by electrically modifying the texture at temperatures close to the liquid crystalline–isotropic transitions, and then cooling the polymer sample down below the temperature threshold, whence removing the applied electric field. The d.c. induced texture showed very little contrast with the unaligned polymer texture (both being highly scattering) but the clear a.c. induced texture provided a very high contrast and the implications of this storage effect are discussed elsewhere[8,15].

It was found that the high contrast storage effect, while being highly stable in the liquid crystalline phase of the polymer, was destroyed irreversibly on cooling below the
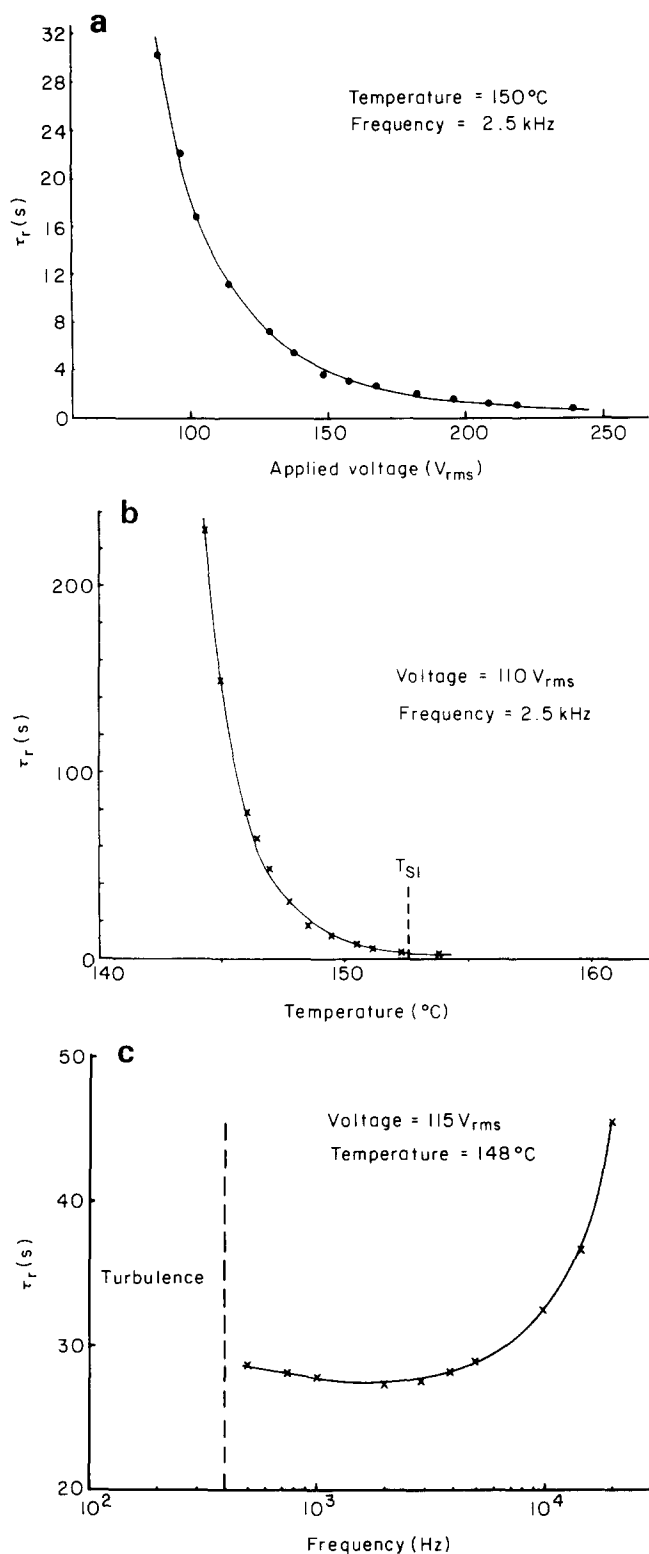

Figure 6 Curves showing the response time (τ_r) variations with (a) sample temperature (b) applied voltage and (c) frequency of electric field. All curves refer to polymer sample A4 and a cell thickness of 25 μm

Table 1 Effect of cell thickness upon the threshold voltage for electro-optic effects in polymer A4. $T = T_{SI} - 3$°C

Cell thickness (μm)	Threshold voltage (V_{rms})
45	300
31	120
25	56
14	25
10	15

crystalline–liquid crystalline transition temperature. If the sample exhibited a liquid crystalline to glass transition, then the high contrast storage effect remained stored. Clearly, the advantage of increased spacer length for lower threshold voltages and faster response times are only useful if the crystallization temperature is below ambient or there is a direct glass transition.

CONCLUSIONS

In conclusion then, the length of the flexible spacer separating the mesogenic moiety from the polymer backbone had a significant effect on both the phase and electro-optic properties of the side chain polymer liquid crystals studied.

Increasing the length of the spacer increased the liquid crystalline–isotropic phase transition temperature and reduced the glass transition temperature (thereby effectively increasing the range of stability of the liquid crystalline phase). Both the tendency towards smectic behaviour and the exhibition of a crystalline phase were enhanced by increasing the spacer length.

Electric field effects seen in the polymers were only readily observed in a limited temperature region close to the liquid crystalline–isotropic transition. These were (i) a d.c. field induced turbulence, which led to a highly scattering texture, and (ii) an a.c. induced realignment ($f > 500$ Hz) which exhibited high optical clarity. Reductions in the threshold voltages, and optical response times for both effects were noted as the spacer length was increased.

The effects of temperature, voltage and frequency of the applied a.c. electric field upon the response times were measured and, together with the cell thickness dependence, lead us to assume that under optimum conditions, the response of side chain polymers can be lowered further from present values of around 200 ms.

The evidence for changes in polymer viscosity, as the liquid crystalline–isotropic phase transition was approached, have been presented via the optical properties of thin polymer films (TOA) and the existence of temperature thresholds below which electro-optic effects were not observed on any meaningful timescale.

That electrically induced textural changes could be durably stored on cooling into the liquid crystalline phase, underlines the importance of the viscosity behaviour of these materials. We are carrying out further work to determine how the material parameters and the viscosity are inter-related.

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