

High-resolution laser-addressed liquid crystal polymer storage display†

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Smectic side chain polysiloxane polymer liquid crystals have been used to demonstrate high-resolution laser writing on thin ($\sim 20 \mu\text{m}$) polymer films. Depending on the pulse energies (typically $< \text{mJ}$), pulse durations ($\leq \text{ms}$) and the optics chosen, thermal laser writing may be achieved on the scale of $10 \mu\text{m}$ or less. The highest resolution so far achieved is $\sim 1\text{--}2 \mu\text{m}$. The parameters that control this will be discussed. The optical effects, manifest as either (a) a clear on scattering texture or (b) the inverse, may readily be stored for long periods (months–years) and show very high contrast ratios ($\sim 10^3:1$). The storage effect is novelly observed above T_g and this has significant ramifications for material synthesis and response characteristics.

(Keywords: liquid crystals; comb-like polymers; electro-optic effects; laser addressing; optical storage)

INTRODUCTION

Polymer liquid crystals, as a class of materials that exhibit intermediate and mobile structures (or mesophases) between the crystalline or glass phases and the isotropic melt, have been recognized for at least thirty years¹. In this early classic work the mesophases were formed on increasing the polymer concentration of helical polypeptides when dissolved in various organic solvents. Such mesophases are called *lyotropic*. Recently polymer mesophases have been observed, in the absence of solvent, as a function of temperature. Such mesophases are called *thermotropic* in analogy with low molar mass liquid crystal materials². Two main types of thermotropic liquid crystalline polymers have been recognized: (a) main chain, in which the mesomorphic polymers are generally formed by chemically linking low molar mass liquid crystals head to tail to form a long thin polymer chain^{3–5}, and (b) side chain, in which low molar mass liquid crystals are chemically linked as pendant side groups to a flexible or semi-flexible backbone to give a comb-like polymer^{6,7}.

Technological interest has developed in the main chain polymer mesogens because of their potential use in the production of ultra-high modulus fibres. In such systems the polymer is spun, in its fluid mesophase, to produce a high degree of polymer order, and strength, along the axis of the resultant fibre. In the side chain systems the viscoelastic properties of the polymer backbone are combined with the electro-optic properties of the pendant low molar mass liquid crystals. In a number of recent studies^{8,9} electro-optic effects similar to low molar mass liquid crystals have been observed in nematic side chain polymer liquid crystals. However, the high viscosities of the polymer, several orders of magnitude greater than their low molar mass counterparts, would appear to limit their usefulness for practical displays. Nonetheless, it has been shown that such electro-optic effects may be stored below

T_g , the polymer–glass transition¹⁰. This would appear to be the main use of such pure nematic polymer materials, i.e. in the storage of optical information.

The main disadvantage of below T_g storage lies in the high temperatures ($\sim 120^\circ\text{C}$) implicit in the device before the optical information can be electrically written. We have recently shown^{11–13}, for the first time, how the smectic phase exhibited by suitable side chain polymer liquid crystals may be used to store similar optical information above T_g . This had the advantage of lowering the operating temperature of the device to $\sim 10^\circ\text{C}$ – 20°C above ambient. In the current paper we will review elements of this storage work in order to demonstrate how we have achieved novel high resolution laser written optical storage effects in such polymer samples.

EXPERIMENTAL

Materials

The samples studied were smectic polysiloxanes with mesogenic segments based on the successful cyanobiphenyl low molecular weight units. The chemical structure and phase transitions of the polymers are given in *Figure 1*. The nomenclature used relates to previous measurements in these polymers^{12,13}.

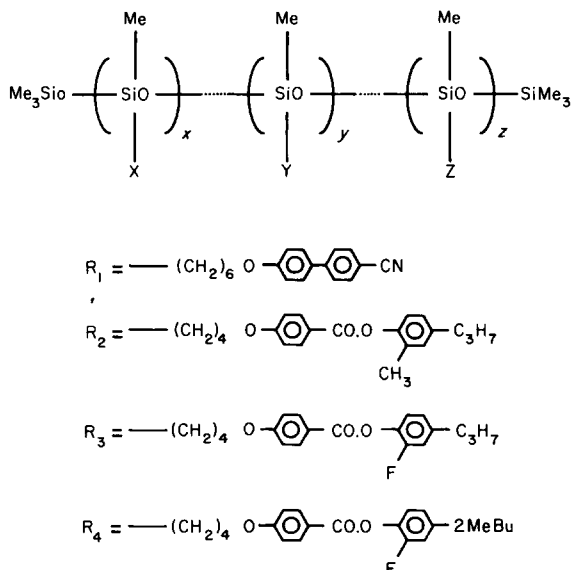
Both the polymers and transition data were kindly supplied to us by Professor G. W. Gray FRS, Dr D. Lacey and Dr P. A. Gemmell of Hull University¹⁴. The average degree of polymerization of all samples was 50, the polymers thus had a molecular weight of 1.8 to 2.2×10^4 daltons. Since the polymers had already been purified prior to dispatch, no further cleaning was attempted.

Cell preparation

A typical sample cell is shown schematically in *Figure 2a*. The substrates are 1.5 mm thick glass plates coated with a thin transparent conductive In/SnO_2 film to allow the application of electric fields across the polymer samples, parallel to the viewing direction. Separation of the substrates is achieved by sandwiching the two plates

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| POLYMER | X | Y | Z | x | y | z | Phase transitions |
|---------|----------------|----------------|----------------|----|------|-----|-------------------|
| PG253 | R ₁ | - | - | 50 | - | - | g28.3s132.5i |
| PG296 | R ₁ | R ₂ | - | 25 | 25 | - | g4.0s85.9i |
| PG278 | R ₁ | R ₃ | R ₄ | 25 | 22.5 | 2.5 | g0.5s121.7i |

Figure 1 Chemical structure and phase transition temperatures (in °C) of the smectic polymer samples

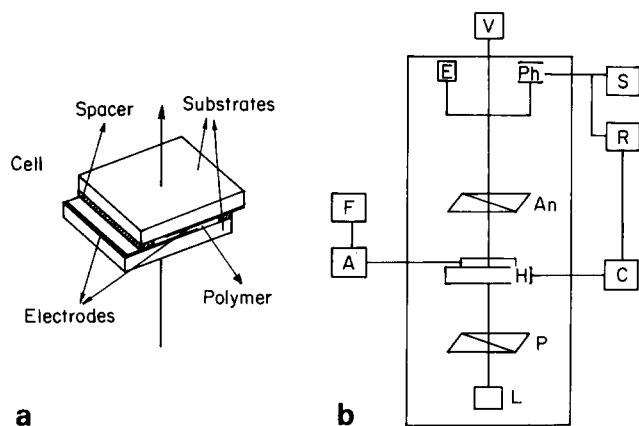


Figure 2 (a) A magnified drawing of a typical sample cell and (b) a schematic diagram of the apparatus used to study the polymer liquid crystal samples (F, function generator; A, amplifier; H, hot stage; C, controller; R, chart recorder; S, storage scope; Ph, photodiode; E, eyepiece; V, video-camera; An, analyser; P, polarizer; L, lamp)

with an adhesive spacer, thus also defining the thickness of the polymer film. The empty cells were filled with the chosen polymer by capillary action at a temperature above the liquid crystalline-isotropic phase transition. Prior to assembly, electrode patterns were etched onto each substrate to predefine an active, electric field addressable area within the bulk polymer film. The same cells were also used to demonstrate the high resolution laser writing.

Apparatus

The polymers were studied using a hot stage polarizing microscope adapted as in Figure 2b. In addition to the direct viewing facility, a camera/video attachment enabled textural and phase transitions to be recorded, whilst

a linear response photodiode mounted in one of the twin eyepiece tubes was used to monitor any transient optical changes accompanying the application of electric fields across the samples. These were recorded using either a storage oscilloscope or chart recorder. Electric fields of variable strength and frequency were supplied by a function generator via a linear high voltage amplifier (Electro-Optic Developments model LA-10A).

RESULTS

Thermo-optic analysis

The liquid crystalline-isotropic phase transitions of the polymers studied were verified on the hot stage microscope both visually and by a technique of thermo-optic analysis (t.o.a.) which monitors the transmission of the polymer sample between crossed polars as a function of temperature. Visually, the first appearance of the isotropic phase in the smectic polymer samples was taken as the smectic to isotropic (S-I transition temperature). Figure 3 shows the result of t.o.a. on the polymer sample PG296. At room temperature the polymer film showed a highly scattering (opaque) texture which thus gave a low transmitted light intensity. As the S-I transition temperature was approached, the light transmission increased drastically due to the appearance of a highly birefringent and fluid texture, whilst above the S-I transition, the appearance of the isotropic phase (which gives extinction between crossed polars) reduced the transmission to zero. The photomicrographs of Figure 4 show typical polymer smectic textures for PG296 at temperatures just below and just above the S-I transition.

Electric field effects

The threshold voltage (or electric field) at which optical or textural changes were seen in the samples was critically dependent on the temperature. For example, at temperatures below 70°C for PG 296, electric fields of magnitude $2 \times 10^7 \text{ V m}^{-1}$ and larger induced no change in texture over periods of several minutes. At temperatures above 70°C, however, both the threshold electric field and the time taken for the polymer to respond to the field were reduced as the temperature was increased up to around 88°C. Typically, a field of $5 \times 10^6 \text{ V m}^{-1}$ (50 Vrms across a 10 μm layer), applied at 85°C caused an optical response time of around 1 second. Obviously, higher electric fields (whether by increasing the voltage or by reducing the layer thickness) will lead to subsecond response times, and this has been reported¹⁵. The strong link between the thermo-optic curve and electro-optic behaviour (in terms

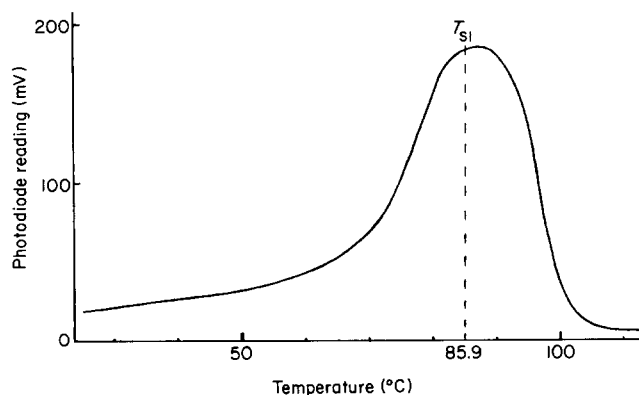


Figure 3 Thermo-optic analysis (t.o.a.) of polymer PG296

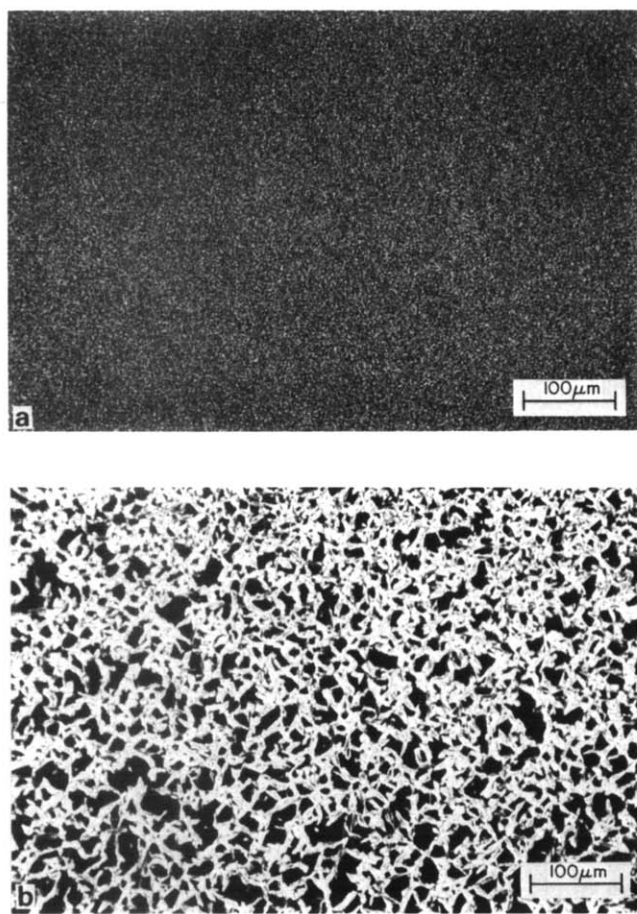


Figure 4 Photomicrographs taken between crossed polars showing (a) a typical polymer smectic texture, PG296, 84°C, and (b) a two phase (smectic + isotropic) texture after annealing for a few minutes at 88°C. Original magnification $\times 100$

of threshold and response) was also seen in the other two polymers studied (PG253 and PG278).

Microscopically, the textural changes on applying an electric field across a sample, can be divided into two classes depending on the frequency of the applied field. At low frequencies (300 Hz and below) application of an electric field above the threshold induced a turbulence in the sample leading to an increase in light scattered and consequently a reduction in transmission as seen between crossed polars. *Figure 5* shows the effect of a 200 V d.c. electric field applied across a 30 μm layer of polymer PG253 at 133°C. The active cell area is shown in the bottom left hand corner A of *Figure 5b*, the electrode edge being indicated by the broken line.

At frequencies above 300 Hz no turbulence was seen. Instead, homeotropic alignment of the mesogenic side groups in the direction of the electric field occurred. This led to an optically clear texture (region H) which showed extinction between crossed polars (*Figure 6*). The evidence for the homeotropic alignment came from optical conoscopy, which gave a positive uniaxial interference figure for the aligned area. This did not change as the sample stage was rotated. All three polymers exhibited this high frequency homeotropic realignment of the mesogenic segments.

For both of the electrically induced effects described above, storage of the induced textures was effected by cooling the sample to a temperature some 15°C below T_{S1} and then removing the applied electric field. Since the

polymer naturally exhibited a scattering texture at low temperatures, the d.c. induced texture provided little contrast. The high frequency a.c. induced homeotropic texture, on the other hand, provided a high optical clarity and an ultra high contrast effect with respect to the scattering non-field aligned texture. This is shown in *Figure 7*, where visual information has been photographed through an electrically aligned stored polymer sample (b). The contrast provided is some 10 or more times higher than that seen in conventional low molecular weight smectic systems^{11,13}.

As can also be seen from *Figure 7*, the addition of a dichroic dye to the sample (a) had very little effect on the

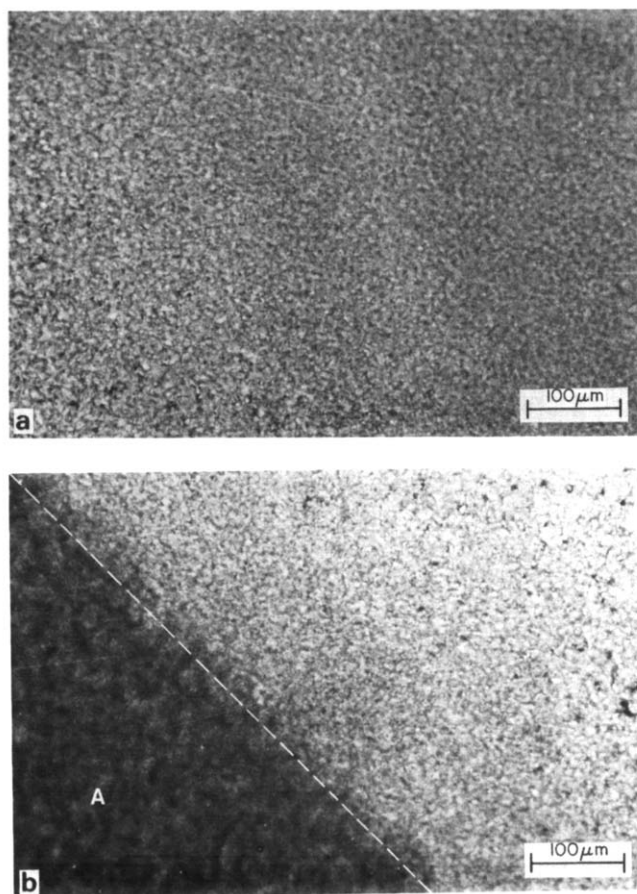


Figure 5 Texture of PG253 (a) prior to, and (b) after the application of 200 V d.c. across a 30 μm layer. (Active cell area A is in the bottom left hand corner) $\times 100$

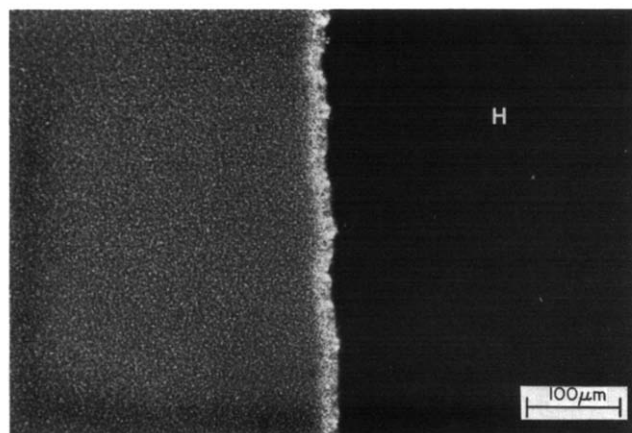


Figure 6 Homeotropically aligned texture (H) produced in PG296 by the application of a high frequency (2 kHz) a.c. electric field. $T = 84.6^\circ\text{C}$, $V = 150 \text{ V}_{\text{rms}}$ and cell thickness = 30 μm

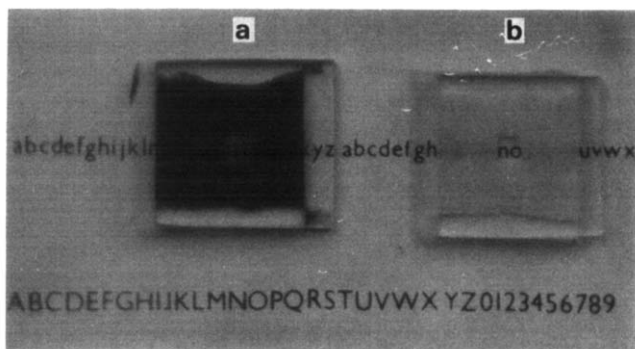


Figure 7 Photograph showing the high optical clarity of the stored, electrically aligned, homeotropic polymer texture. Cell thicknesses = 30 μm . (a) Dyed, and (b) undyed polymer samples. Note also the high contrast provided by the scattering texture

high contrast storage effect, indicating that the dye molecules had become cooperatively aligned with the mesogenic side groups of the polymer. This, as will be discussed later, has important implications on laser induced textural changes.

Response times

The response of the polymer films to various applied electric fields as a function of frequency, voltage and temperature was studied for the scattering to clear (induced homeotropic) transition. The response time (τ_r) was defined as the time taken to reduce the transmitted light intensity, between crossed polars, to 10% of its initial value. Typical results for the polymers under investigation are indicated in *Figure 8*, which shows (a) the frequency dependence of τ_r for PG278, (b) the temperature dependence of τ_r for PG253 and (c) the voltage dependence of τ_r for PG296, all other variables being held constant. The shape of the frequency, temperature and voltage dependence of the rise time was similar for all of the polymers studied, i.e. (i) optimum response times were observed in the frequency region 1–4 kHz, (ii) a large reduction in response time occurred as the temperature was increased, and (iii) the response time had a strong voltage dependence, $\tau_r \propto V^{-3.5}$.

Under equivalent relative conditions of temperature and cell thickness, the voltage response of the three polymers was very nearly equal and, under optimum conditions, response times as low as 200 ms were observed. These times are quite comparable to those seen in low molecular mass smectics¹⁶, belying the fact that the viscosity of the polymers is apparently several orders of magnitude greater than the low molar mass systems. We are currently studying this viscosity behaviour in greater detail.

Laser-addressed storage effects

From the above results, it is clear that essentially two different optical textures can be induced in polymer liquid crystals using thermal or electric fields and that both textures can be durably stored at temperatures well above the glass transition. In the case of PG253 for example, storage has been observed between ambient and 110°C. Furthermore, the field induced clear homeotropic texture can be reversed, i.e. changed back to a scattering texture, simply by heating the sample above T_{S1} and allowing it to cool in absence of an applied field. Based on this mechanism, we realised that if a laser beam could be used

as the heat source then we had a method of producing a high contrast, high-resolution (i.e. diffraction limited) addressable storage display that could be refreshed using a combination of suitable thermal and electric fields. In this section we report preliminary results of studies on laser-addressing in smectic side chain polysiloxanes.

The initial experiments were carried out on a homeotropically aligned sample of pure PG296 at room temperature. An air-cooled Argon-ion laser providing 25 mW at 514.5 nm was focused down onto the clear, electrically written texture of the polymer liquid crystal by means of a

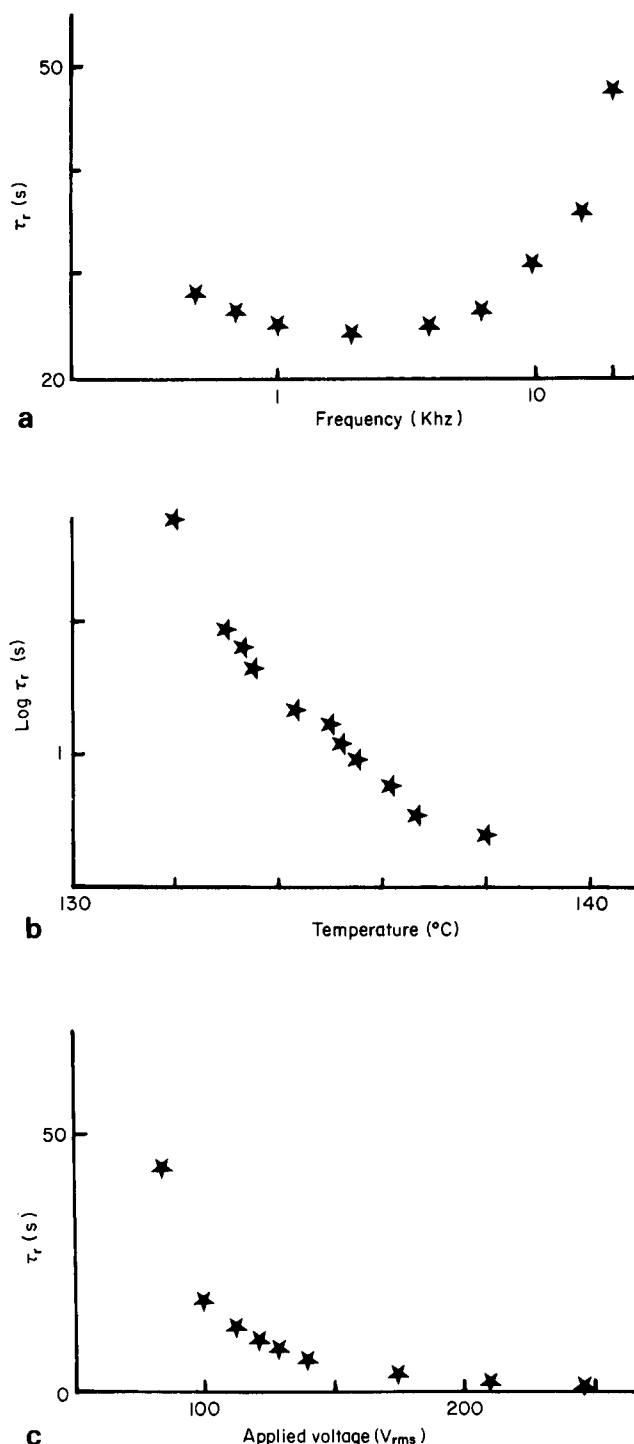


Figure 8 Variation of response time, τ_r , with (a) frequency of the applied electric field—PG278 ($T = 117^\circ\text{C}$, $V = 100 V_{rms}$), (b) the sample temperature—PG253 ($V = 200 V_{rms}$, $f = 2 \text{ kHz}$) and (c) the applied rms voltage—PG296 ($T = 84^\circ\text{C}$, $f = 2 \text{ kHz}$). Cell thickness = 30 μm

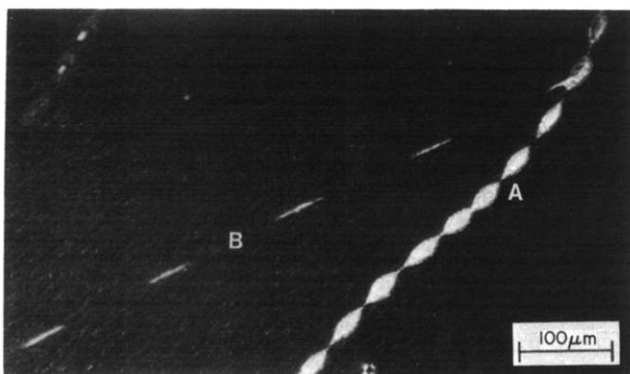


Figure 9 Photomicrograph showing laser written textures (lines A and B) produced by scanning the sample perpendicular to the focused laser beam (background texture is homeotropic) $\times 100$, 25°C . Cell thickness = $30\ \mu\text{m}$

50 mm plano-convex lens. The unfocused laser beam had a diameter of roughly 1.5 mm, which gave a calculated focused beam 'waist' of about $20\ \mu\text{m}$. The sample was moved perpendicularly to the laser beam by means of an X - Y translation stage. *Figure 9* shows the result of a slow movement ($\sim 1\ \text{cm s}^{-1}$) of the sample (line A) relative to the laser beam. The size of the scattering areas produced was around 20 – $25\ \mu\text{m}$, in keeping with the diameter of the focused laser beam. If the sample was moved more rapidly ($\sim 5\ \text{cm s}^{-1}$) then the 'line' became discontinuous (B). In this case the scattering centres had a width of $\sim 5\ \mu\text{m}$, i.e. much less than the laser beam 'waist'. This indicates that high resolution optical effects may be observed with such polymer films although the amount of heat energy absorbed by the polymer limits the rate at which information can be written.

In order to increase the thermal absorption of the polymer film guest dye molecules were dissolved in the host polymer heated into the isotropic phase. These dyed polymers were then aligned, as discussed above, to give either a homeotropic or a scattering texture. The preliminary experiments showed an enhanced absorption of energy, through an improved scanning capability, again at room temperature. Further, as can be seen in *Figure 10*, realignment took place, not only in the clear homeotropic texture, but also in the scattering texture of the polymer film. The width of the line written in the scattering texture was slightly greater than that for the homeotropic texture. This was presumably due to a greater absorption of energy in the former case caused by a predominance of alignment in the sample plane of the guest dye molecules. The textural changes produced by the laser beam were seen to be independent of the background texture, which indicated that the mechanism of realignment was not simply a heating of the sample above its clearing temperature (in which case the laser written line within the scattering texture would not have been readily visible). Macroscopically, the optical density of the laser written track was intermediate to that of the clear homeotropic texture and the highly scattering region. Microscopically, between crossed polars, the laser induced texture was birefringent which implies that the optically anisotropic mesogenic side groups were aligned in a plane perpendicular to the incident laser beam (i.e. in the plane of *Figure 10*). Further a sequence of birefringence colours was observed extending from the outer edge to the middle of the laser written track. This indicated that the alignment increased towards the centre of the track. We,

therefore, examined this feature under greater magnification, *Figure 11*. From these photomicrographs the birefringent texture clearly follows 'frozen' lines in the direction of travel of the laser beam across the sample. Further, the alignment of these textures appears to be complete at the centre of the track. These thermally induced effects were independent of the polarization plane of the incident laser light since no differences were observed for a beam polarized parallel or perpendicular to the scan direction. Therefore, in this instance, laser field induced orientation processes can be ignored. In order to explain the flow alignment, it is necessary to consider the distribution of energy in the laser beam. Since the intensity distribution across the beam was gaussian, the temperature profile across the track, due to the dye absorption, would also have been gaussian with a higher temperature at the centre than at the edges. Therefore, on cooling (on displacement of the laser beam) the outer edges would have undergone the isotropic to smectic transition first followed by the higher temperature region at the centre. The density changes, commensurate with this temperature gradient, would then have caused the material to flow towards the region of highest temperature (or in the scan direction) during the writing process. Further, due to the viscosity decreasing with increased temperature in the fluid, biphasic and isotropic phases respectively, the flow effect would have been enhanced at the beam centre. Hence the flow like appearance of the texture finally stored in the smectic phase. Whilst this hypothesis has yet to be verified by high speed optical recording, it seems the most likely explanation of these novel laser induced textures.

All of the above measurements were carried out at room temperature which, in the case of PG296, implies a temperature jump in the sample of more than 50°C . Clearly, improvements could be made by temperature biasing the sample or by decreasing the temperature of the smectic to isotropic phase transition. Further improvements could be obtained by matching the absorption peak of the dye to the input laser and by increasing the dye concentration. The use of dye containing copolymers might be envisaged and all of these changes should lead to considerably improved writing times and sensitivities. Finally, it is worth reiterating that all of the laser induced textures could be reversed on heating the samples above T_{S1} and allowing the sample to cool either without a field (scattering texture) or with a high frequency field to give a clear homeotropic alignment.

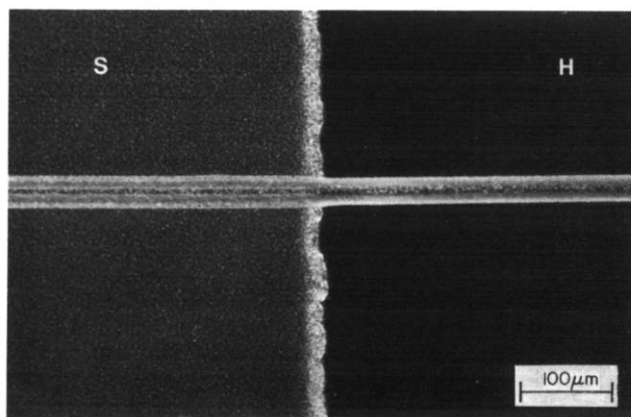


Figure 10 Laser written line within the homeotropic, H, and scattering, S, textures of a dyed sample of polymer PG296 $\times 100$, 25°C . Cell thickness = $30\ \mu\text{m}$

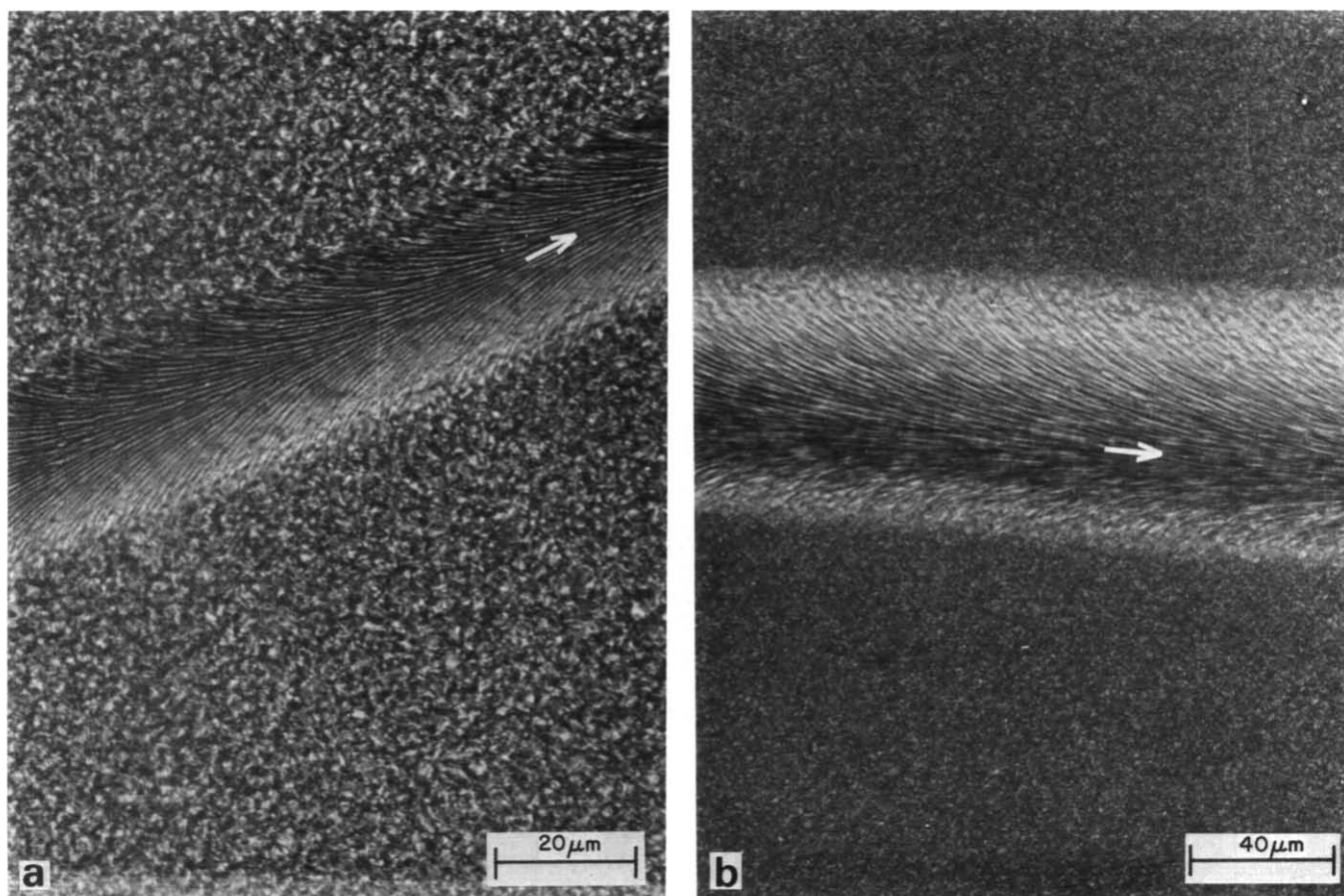


Figure 11 Photomicrographs clearly showing evidence of flow alignment produced by the passage of a focused laser beam across the scattering textures of dyed samples of PG296: (a) magnification $\times 400$. (b) magnification $\times 200$, 25°C . Sample thickness = $30\ \mu\text{m}$. The arrows indicate the laser scanning direction

CONCLUSIONS

We have shown that both opaque scattering and clear homeotropic textures may be induced in smectic side chain polymer liquid crystals and that these textures may be readily stored above T_g in the smectic phase. The conditions for optimizing the response times for such polymers have been discussed in terms of temperature and applied voltage and frequency of the applied field. Using these smectic polymer textures, we have shown how high resolution and high optical contrast laser writing may be obtained in both undyed and dyed (guest–host) polymer systems. Such optical effects have been readily stored for long periods of time (~ 2 years) in the smectic phase and are therefore extremely durable. Further, they may be thermally and electrically erased, and are laser written at room temperature. This is in marked contrast to a recently reported study in a nematic side chain polymer material¹⁷ where it was necessary to temperature bias the sample to within 1 degree of the nematic–isotropic transition (106°C) to obtain laser writing, and where the spatial resolution achieved was only $150\ \mu\text{m}$. We, therefore, believe that such materials demonstrate a new and rewarding area of research and application for these new speciality polymers.

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