Electrically-induced optical storage effects in smectic polysiloxanes A variable transmission device

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Electrically-induced optical storage effects in smectic polysiloxanes
A variable transmission device

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Changes in the optical transmission induced by electric fields have been studied in a smectic side-chain polysiloxane liquid crystal. The transmission varied from effectively zero, for a highly scattering (opaque) texture, to total, for a homeotropic texture, on increasing the applied voltage across the material. The field-induced textures were durably stored in the smectic phase, enabling the order parameter of the side groups to be studied by dielectric relaxation measurements. For the highly transparent texture, a side group order parameter of 0·92 has been observed.
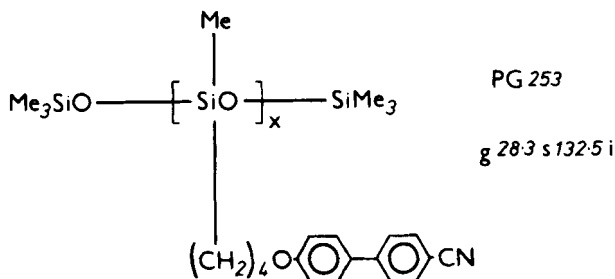
1. Introduction

Thermotropic liquid crystal polymers with mesogenic side groups have been the subject of much research in recent years. As implied by their name, these materials show both polymer-like properties, for example, a glass transition temperature, T_g, below which bulk molecular motions are frozen, and liquid-crystalline properties, for example, at temperatures above T_g, the side groups form mesophases which can be cooperatively aligned by electric or magnetic fields. The presence of the glass transition, which is pseudo-second order, means that electrically induced liquid-crystalline textures can be durably stored by cooling the sample below T_g. Recently however, we have reported electro-optical storage effects in smectic polysiloxane liquid crystals at temperatures well above the glass transition [1]. Thus these materials show considerable promise in the optical/data storage fields both at temperatures below T_g or in the smectic phase. As previously shown, application of suitable electric fields to the polymers induces optical textures that are highly transparent, and contrast sharply with the opaque, randomly aligned polymer texture obtained by cooling from the isotropic melt. Optical evidence indicated [2] that the cyanobiphenyl side chains were aligned parallel to the applied electric field and exhibited a positive uniaxial behaviour. The high optical clarity of these textures implies a high-order parameter, S of the mesogenic side groups, indeed S values of 0·85 $\pm$ 0·05 [3] and 0·92 [4] have been observed in the glassy state of aligned smectic polyacrylates with mesogenic side groups.

Here we report a method of controlling the bulk optical transmission of thin ($\simeq 6\,\mu$m) layers of a smectic side-chain polysiloxane using an applied but variable electric field. As we shall show the applied field induces a macroscopic alignment of the smectic domains. Since the alignment changes for various fields from a completely disordered state, through partially ordered to effectively a totally aligned or monodomain material, the optical transmission also varies in a well-controlled way. For this fully-ordered state the order parameter of the side groups has been determined

from dielectric loss measurements and good agreement is obtained with those values given in [3, 4] for other side-chain polymer liquid crystals.

2. Experimental

The material studied was a homopolysiloxane of 50 repeat units, with cyano-biphenyl side groups, designated PG253, whose chemical structure is

$$
\text{Me}_3\text{SiO} \overline{\quad\Big[\,\overset{\displaystyle \overset{\text{Me}}{|}}{\underset{\displaystyle |}{\text{SiO}}}\,\Big]_x\quad} \text{SiMe}_3
$$

PG 253

g 28·3 s 132·5 i

$$(\text{CH}_2)_6 \text{O} \langle\!\langle \bigcirc \rangle\!\rangle\!-\!\langle\!\langle \bigcirc \rangle\!\rangle \text{CN}$$

The polymer exhibited a smectic–isotropic transition temperature of 133°C, and a glass transition at 28°C.

The polymer samples were contained between two glass plates coated with transparent, conductive indium/tin oxide layer. The cell spacing was maintained at about 6 μm by a non-conducting epoxy adhesive. Samples were observed using a polarizing microscope in transmission, and temperature stability (to ± 0·1°C) was provided via a commercial hot stage and controller. Full details of the apparatus are given in [5]. Electro-optic measurements were obtained by cooling the sample from the isotropic phase, to some 50°C below the smectic–isotropic transition temperature, while being subject to an electric field. Temperature versus transmission curves were obtained simultaneously via an X–Y recorder.

Dielectric relaxation measurements were then performed on the polymer sample using a Wayne Kerr 6425 Precision Component Analyser: the results were interpreted in a similar fashion to those of Kresse and Talrose [6].

3. Results and discussion

The transmission of the polymer sample was monitored between parallel polarizers on the microscope. At low temperatures the prepared polymer film was highly scattering and exhibited a very low intensity of transmitted light. On increasing the temperature the light transmission remained fairly constant up to 115°C. It then increases slightly on further heating to 133°C, where a drastic intensity increase occurred at the transition temperature. Above 140°C, the polymer existed in the isotropic phase and exhibited optical transparency. The intensity of transmitted light in the isotropic phase was taken as 100 per cent, while that of the opaque, unaligned polymer film was assigned a value of 0 per cent. (In practice the transmission of the opaque polymer was small, but non-zero.)

The curves shown in figure 1 were obtained by cooling the polymer from a temperature of 150°C (isotropic phase), at a cooling rate of about 20°C/min, through the isotropic–liquid crystalline phase transition, to a temperature of 90°C, under various applied voltages. Although there was a slight thermal lag of about 4°C between the polymer and the indicated hot-stage temperatures this effect was neglected since all of the curves were recorded under identical cooling conditions. Curves
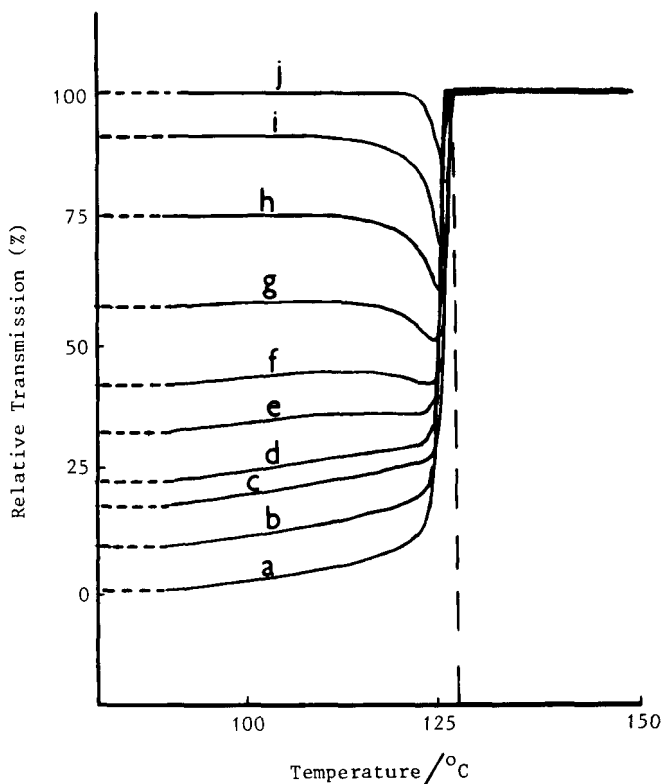
Figure 1. Induced transmission versus temperature curves for the polymer sample, cooled under different applied fields. Curves *a–j* represent applied voltages of 0, 8·1, 10·0, 10·8, 11·6, 12·8, 14·1, 16·7, 20·7 and 28 V_{rms} (at a frequency of 2 kHz), respectively across the 6 μm thick sample.

a–j show the effect of increasing the applied voltages from 0 to 28 V_{rms} (at 2 kHz). The smectic–isotropic phase transition occurred on cooling at 129°C as compared to 133°C for the transition on heating. From earlier work [2], on this particular polymer, electrically-induced textures remain stable, stored at temperatures up to 115°C and show no degradation of their optical properties, thus implying that the applied voltage could have been removed at 115°C without affecting the ultimate transmission of the textures. As can be seen from figure 1, even at high applied voltages (28 V_{rms}), the polymer exhibits a slightly scattering texture on cooling, prior to establishing a high level of transmission. This reflects the slow (several seconds) response of the polymer to applied electric fields. Initially, the disorder induced by cooling through the isotropic to smectic phase transition predominates, giving the slightly scattering texture. On further cooling, the applied electric field aligns the mesogenic side groups predominately perpendicular to the plane of the glass plates, giving a clear homeotropic texture.

Plotting the relative induced transmission of the polymer film as a function of applied voltage produces the data shown in figure 2. Above a voltage of 28 V_{rms}, the transmission saturated at a maximum value. As is evident from figure 2, a very low threshold voltage exists for electrically induced orientation effects. At high cooling rates (and in thicker cells) the voltages needed to induce a specific
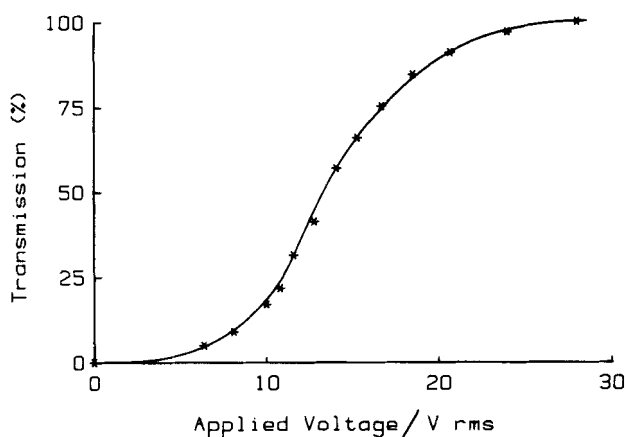
Figure 2.   Relative induced transmission as a function of applied voltage for the same cell as that used for figure 1.

transmission in the sample are raised, and obviously at lower cooling rates the opposite applies.

4.   Dielectric studies

Dielectric relaxation phenomena have recently been studied by us in a highly aligned sample of the polymer [7]. It was assumed that the large electric dipole associated with the cyano group was aligned parallel to the axis of the mesogenic side group (and thus the measuring electric field), and that the observed relaxation process could be assigned to a cooperative rotation of the side groups and polymer main chain on the basis of the temperature variation of the activation energy.

Figure 3 shows dielectric loss curves for the highly aligned sample, the randomly aligned sample, and those for three intermediate samples, at a temperature of 75°C. The aligned sample exhibits a symmetric loss peak, of half width $\simeq 1.4$, in accordance with earlier measurements [7], indicative of a single loss process. The curve for the randomly aligned sample, however, is extremely asymmetric and can be thought of as the superposition of two (or more) competing loss processes. This reflects the random arrangement of the directors (unit vectors describing the local preferred direction of the mesogenic side groups) within the bulk sample, allowing all possible relaxations of the dipole moments to take place. On increasing the degree of alignment of the director, we see a large concomitant increase in the magnitude of the loss process.

According to Maier and Meier [8], the dielectric increment $(\varepsilon_{\parallel}^0 - \varepsilon_{\parallel}^\infty)$ is directly proportional to $(1 + 2S)$, and hence the height of the dielectric loss peak has the same proportionality. Strictly speaking this is only true for Debye-like relaxations, and for non-Debye loss processes we have

$$(\varepsilon_{\parallel}^0 - \varepsilon_{\parallel}^\infty) = 2C''_{max}/(1 - \alpha),$$

where α is the value of the Cole–Cole parameter ($\alpha = 0$ for a Debye relaxation). Cole–Cole plots for the disordered and ordered samples reveal similar values of α ($\simeq 0.12$) for all degrees of ordering, thus the magnitude of the loss process is still directly proportional to $(1 + 2S)$.

Close inspection of figure 3 reveals that on going from the randomly aligned sample to the fully aligned sample, the magnitude of the loss process increases by a
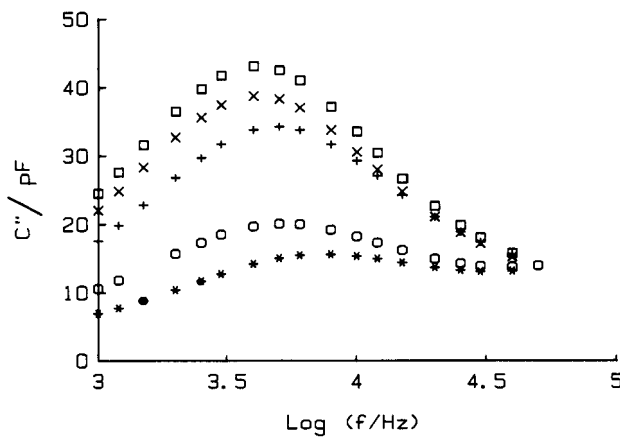
Figure 3. Dielectric loss as a function of frequency, f, measured at 75°C, for the polymer sample, of thickness 6 μm, electrically aligned with applied voltages of: $\square$, 28 V_{rms}; $\times$, 16·7 V_{rms}; $+$, 13·7 V_{rms}; O, 8·1 V_{rms}; and $*$, 0 V_{rms}.
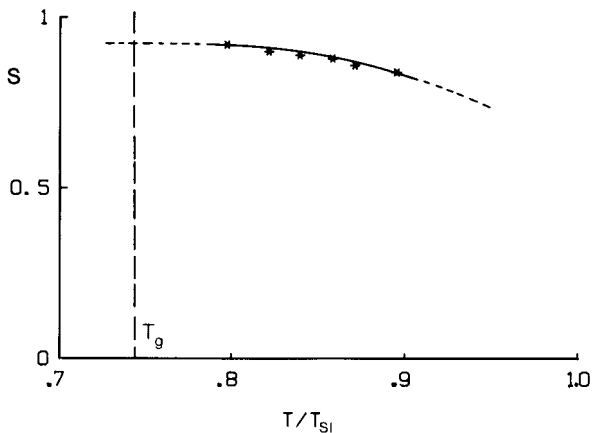
Figure 4. The estimated side group order parameter as a function of reduced temperature (T/T_{SI}) in a highly aligned polymer sample ($V_{applied}$ = 50 V_{rms} at 2 kHz). The sample thickness was 6 μm.

factor of 2·76 leading to an order parameter of 0·88. This value is comparable to the values obtained by Boeffel *et al.* [3] and Wasmer *et al.* [4], under similar conditions of alignment. In principle it should be possible to obtain an estimate of the degree of director alignment from this dielectric data. Since the order parameter, S, of the side groups should be the same in the disordered, partially ordered, or fully ordered homeotropic state we can postulate that the observed dielectric increment ($\varepsilon_{\parallel}^{0} - \varepsilon_{\parallel}^{\infty}$) will be proportional to S. θ, where θ defines the normalized orientational order of the director. In this model $\theta = 0$ for the random disordered smectic phase and has a value of unity for the aligned homeotropic state. We are now examining suitable models for the evaluation of θ from such dielectric data.

The temperature variation of the side group order parameter, in a highly aligned homeotropic state ($V_{applied}$ = 50 V_{rms}) was also estimated according to this procedure, and is depicted in figure 4. The value of S drops slowly from 0·92 at 50°C, to 0·84 at

90°C (the estimated errors are ± 0.02). Estimates of S outside this temperature range were unfortunately not possible because of limitations imposed by the frequency range of the capacitance bridge. The values obtained, however, indicate that the order parameter in these side-chain smectic polymers is at least as high as that found in low molecular mass smectic A systems. This explains the high optical contrast previously reported in the polymer materials of references [1, 2, 5].

In conclusion, we have demonstrated variable transmission storage effects in a smectic polysiloxane liquid crystal. The increased transmission was reflected in a high measured order parameter for the liquid-crystalline side chains, and in highly aligned systems, an order parameter of 0.92 was observed in the smectic phase.

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