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G. Scherowsky[a]; A. Beer[a]; H. J. Coles[b]
[a] Institut für Organische Chemie, Technische Universität Berlin, Berlin, Germany [b] Physics Department, University of Manchester, Manchester, England

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A coloured ferroelectric side chain polymer†

by G. SCHEROWSKY*‡, A. BEER‡ and H. J. COLES§
‡ Institut für Organische Chemie, Technische Universität Berlin,
Straße des 17 Juni 135, D-1000 Berlin, Germany
§ Physics Department, University of Manchester,
Oxford Road, Manchester M13 9PL, England

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Coloured ferroelectric liquid-crystalline side chain copolymers containing 5 per cent and 15 per cent of an azo dye were synthesized and characterized by DSC, GPC and optical microscopy. Order parameters, S, of the azo compound exceeding 0·8 were measured in the frozen smectic phase for the 5 per cent copolymer. The copolymers exhibit fast electrooptic switching in the range of a few hundred microseconds to milliseconds in the S_C^* phase. Both linear (i.e. electroclinic-like) and ferroelectric switching have been observed. Tilt angles of ~19° and spontaneous polarization of $\sim 300\,\mathrm{nC\,cm^{-2}}$ have been recorded in the S_C^* phase.

1. Introduction

Research in ferroelectric liquid crystals has been intense over the past few years. One important advantage of ferroelectric displays compared with the well-known and widely used twisted nematic or supertwist nematic displays is the fast electrooptic switching which is in the range of microseconds. Recently the first examples of switchable ferroelectric liquid crystal side chain polymers have been reported [1–4]. In favourable cases [3, 4] we found response times in the range of some hundred microseconds. Because of the relatively poor anti-shock characteristics of surface stabilized low molar mass ferroelectric display devices fast switching ferroelectric liquid crystal polymers, which form robust films, may find future applications using various birefringent or absorption based electrooptic effects.

Coloured liquid crystal displays applying the guest host effect of dichroic dyes dissolved in a nematic liquid crystal were developed some years ago [5]. Recently the guest host effect of dichroic dyes in a ferroelectric liquid crystal [6] and, for the first time, in ferroelectric liquid crystal polymers has been investigated [7]. One drawback to this effect is the poor solubility of dyes in both low molar mass and polymeric liquid crystal materials. By copolymerization of dye monomers a higher percentage of dye content has been achieved in nematic polymers [8]. Ferroelectric liquid crystal dye copolymers, hitherto unknown, might be expected to have both fast switching properties, associated with the ferroelectric phase, and high colour contrast in thin films, because of the higher order parameter and solubility of suitable dyes in the smectic S_C^* layers.

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* Author for correspondence.

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2. General part

2.1. *Ferroelectric liquid-crystalline dye copolymers*

The aim of this work was to introduce a dye monomer into our recently synthesized fast switching ferroelectric polymer **I** (see figure 1) to give a ferroelectric dye copolymer. The main questions were:

- (i) Is it possible to maintain the ferroelectric properties of polymer **I** when incorporating a dye monomer and to achieve a fast switchable coloured display?
- (ii) How do the properties of the dye containing copolymer depend on the dye content?

For our initial investigations the azo dye **II** was synthesized in a three step procedure analogous to the pathway published by Ringsdorf *et al.* [8] (see figure 2). The synthesis of the ferroelectric monomer has been published elsewhere [9]. Copolymers containing 5 wt% and 15 wt% of the dye monomer were synthesized by copolymerization in toluene with AIBN. The copolymers were investigated and compared with the ferroelectric homopolymer obtained under identical conditions (see table 1).

The homopolymer and copolymer containing 5 per cent of the azo dye monomer show nearly identical transition temperatures. Any reduction due to dye addition appears to be compensated for by the slight increase in the molecular weight of the copolymer. As we discuss later the lower viscosity of the 5 per cent dye copolymer allows electrooptic switching to take place at lower temperatures in comparison with the homopolymer.

The copolymer containing 15 per cent of the azo dye shows a strong effect of the incorporated guest molecule. Despite the higher molar mass of the copolymer (almost twice that of the homopolymer) the transition temperatures decrease, and, as will be discussed further, the electrooptic switching starts at ~60°C in comparison with ~80°C for the homopolymer. In table 1 an apparent transition S_X–S_C^* has been identified; this was achieved by optical microscopy and is not evident in the DSC data. A similar apparent transition has been observed previously [3] and we discuss this later.

2.2. *Electrooptic switching properties*

The electrooptic switching times of the homopolymer and the two copolymers (5 per cent and 15 per cent dye, respectively) are given in figures 3, 4 and 5 respectively.

Electrooptic switching of the 5 per cent dye copolymer starts at ~76°C and the response time ($\tau = 10$ to 90 per cent using crossed polarizers) decreases from 9 ms at 76°C to 1·5 ms at ~100°C (see figure 4). In this temperature range the response time is independent of voltage (up to fields of ~4 $V_{rms}/\mu m$). Application of a triangular waveform reproduced a triangular optical response. Both these results are consistent with an electroclinic switching process [10]. Further, the induced tilt angle θ_t was linearly dependent on the applied field. At ~100°C the S_C^* phase could be clearly identified and the response times became voltage (or field) dependent. As shown in

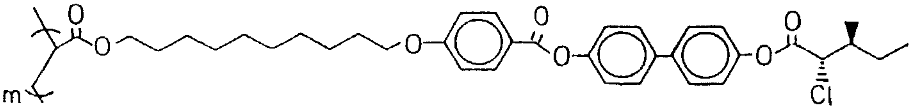

Figure 1. Ferroelectric homopolymer I.

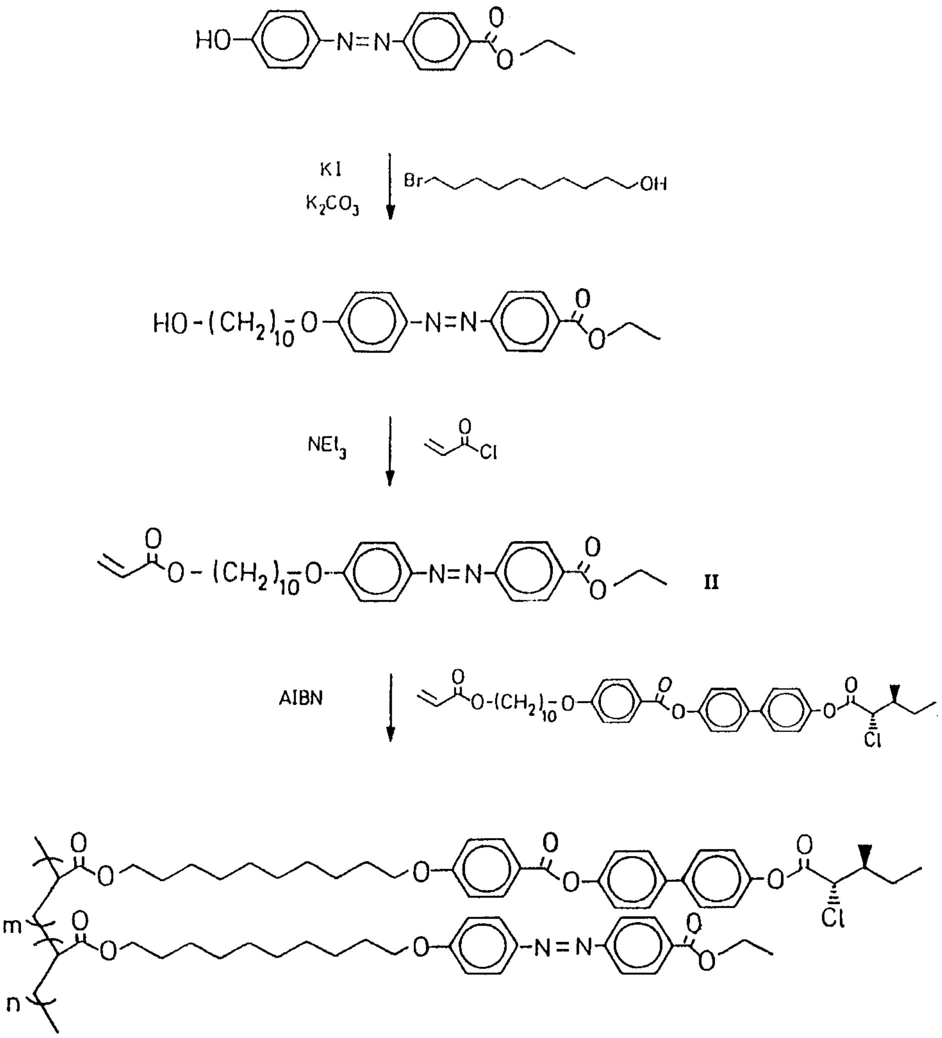

Figure 2. Synthesis of the azo monomer **II** and copolymers.

figure 4, between ~ 100°C and 115°C the response time for the lower voltage is shorter than for the higher voltage. This seems paradoxical since in a S_C^* phase we should expect the response time to be inversely proportional to the applied field. However, in this case the lower voltage corresponds to an electroclinic-like switching (i.e. τ independent of E and an applied triangular wave producing a triangular optical response) whereas the higher voltage is more reminiscent of ferroelectric switching. At the higher temperatures and voltages the tilt angle is no longer linearly dependent on E and the electrooptic switching tends towards a latching between two states. Similar results were obtained for the 15 per cent copolymer and this point is returned to later. At 120°C very short response times of 400 μs were measured at 2·5 $V_{rms}/\mu m$ in a 4 μm thick cell. Above 135°C high fields tended to induce a slight decomposition of the copolymer and so data were not taken in this high temperature region.

The electrooptic switching of the 15 per cent dye copolymer started at ~ 60°C and continued up to ~ 140°C (see figure 5). At 60°C the response time was independent of

Table 1. Polymer properties.

	Homopolymer	Copolymer 5 per cent dye	Copolymer 15 per cent dye
M_w	10 900	14 600	19 300
$E=\frac{M_w}{M_n}$	1·24	1·39	2·33
Mesophases and transition temperatures	g 75°C S_X 100°C S_C^* 140°C S_A 200°C I	g 75°C S_X 100°C S_C^* 140°C S_A 205°C I	g 60°C S_X 94°C S_C^* 110°C S_A 190°C I
Optical switching	20 ms (80°C)–1 ms (138°C)	10 ms (76°C)–400 μs (120°C)	30 ms (60°C)–below 100 μs (140°C)

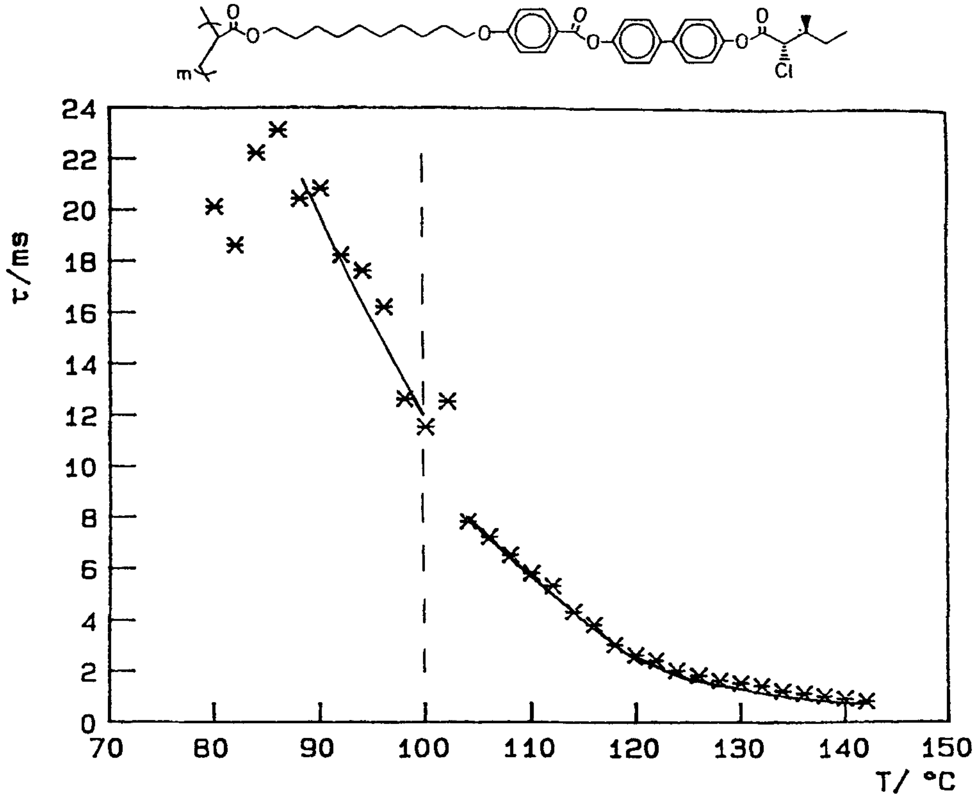

Figure 3. Homopolymer: response time τ versus temperature (sample thickness 4 μm).

voltage at some 32 ms. On increasing the temperature to ~90°C the switching remained independent of voltage, for fields up to ~9 $V_{rms}/\mu m$, and reduced to 2 ms at this temperature. At these fields the electrooptic response was again electroclinic-like or linear in the applied field (i.e. a triangular optical response was recorded for an applied triangular wave) even though these temperatures are well below the S_C^*–S_A transition temperature. Between 90°C and 110°C the response time is again field dependent. The S_C^* phase was clearly visible from the microscopic texture at 94°C. As for the 5 per cent copolymer higher fields induced longer response times and the electrooptic response became ferroelectric (i.e. latching occurred). Above ~110°C, i.e. in the S_A phase, the switching again became electroclinic-like and the response times were independent of applied field. At 110°C the response time was less than 1 ms and decreased to well below 100 μs at 130°C. At low fields (i.e. below ~9 $V_{rms}/\mu m$) apparent electroclinic behaviour was observed both in the S_C^* and S_A phases (see figure 6). From below the supposed S_X–S_C^* transition (at ~90°C) up to the S_A phase (at 110°C) the electrooptic response was linear in the applied field. As shown in figure 6 at low fields the induced tilt angle was linear in *E*. As shown by the dashed line, at high fields, and well into the S_C^* phase, the dependence became non-linear. As shown by the inset, at constant field, the induced tilt angle showed a cusp-like behaviour between 80°C and 110°C. This is typical for a S_C^*–S_A transition. The induced tilt angles are somewhat higher than those induced in low molar mass compounds [10] although the response times are of the order of milliseconds rather than microseconds. For the polymers the electroclinic coefficient was ~1–2 ($\times 10^{-6}$ °m/V_{rms}).

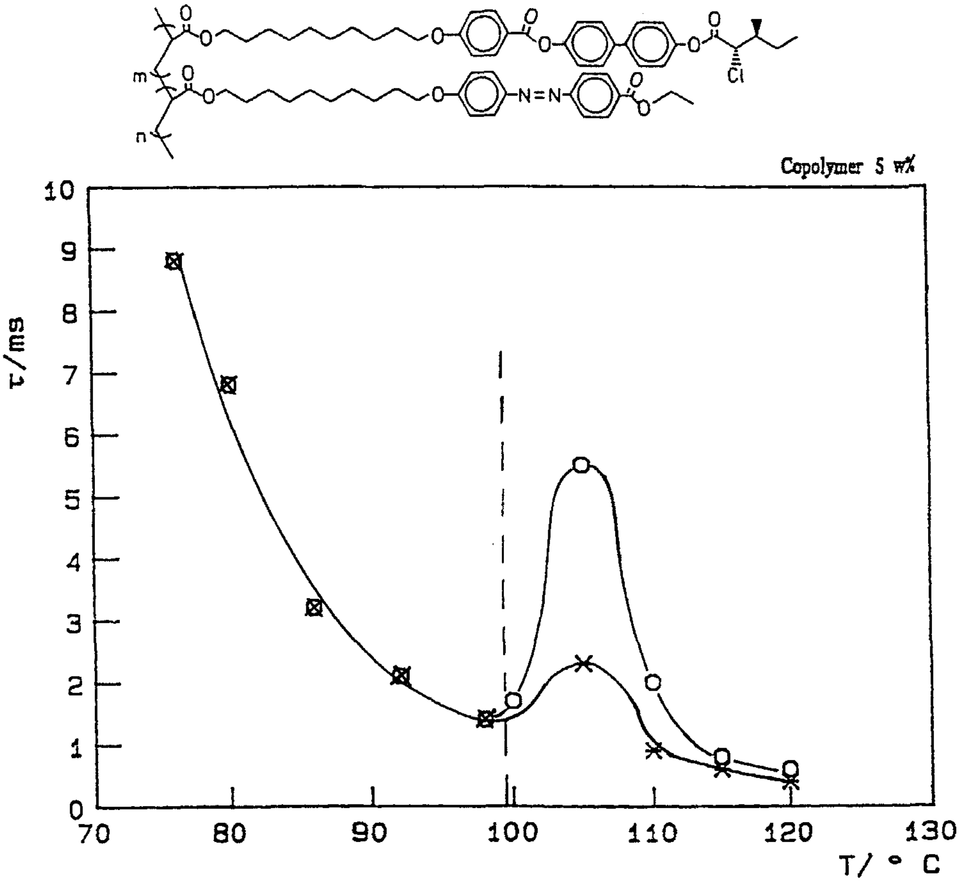

Figure 4. Copolymer (5 per cent): response time τ versus temperature (sample thickness 4 μm). ○ ≙ 4 V/μm; × ≙ 2·5 V/μm.

At low fields, in the temperature range 90°–105°C, it was not possible to measure true spontaneous polarization. As might be expected for electroclinic-like effects the polarization does not show hysteresis and is linearly dependent on the applied field. However, at high fields ($E = 25\,V_{rms}/\mu m$) the spontaneous polarization became independent of E and did saturate as did the induced tilt angle (see figure 7). At these fields true ferroelectric switching was observed; the values of P_S and θ_t were similar to those previously recorded for the homopolymer [7]. As previously recorded the temperature dependence of P_S is unusual in that it decreases with decreasing temperature whilst θ_t increases. We shall discuss this in greater detail in a later paper although this effect is likely to be related to the phase transition occurring at 60°C for this system, coupled to the sample's polydispersity. What is more significant in figure 7 is that ferroelectric switching is observed, at sufficiently high fields, well below the supposed S_X–S_C^* phase transition (at ~90°C). Clearly since the optical texture and the sample's birefringence both alter at this temperature some local reorganization must take place. It is our belief that this effect is due to the helical pitch changing markedly on reduction of the temperature. Thus high voltages are required to unwind the helix at these lower temperatures. This gives the appearance of a phase transition and at low voltages the electroclinic or linear effect can be attributed to the deformed helix mode

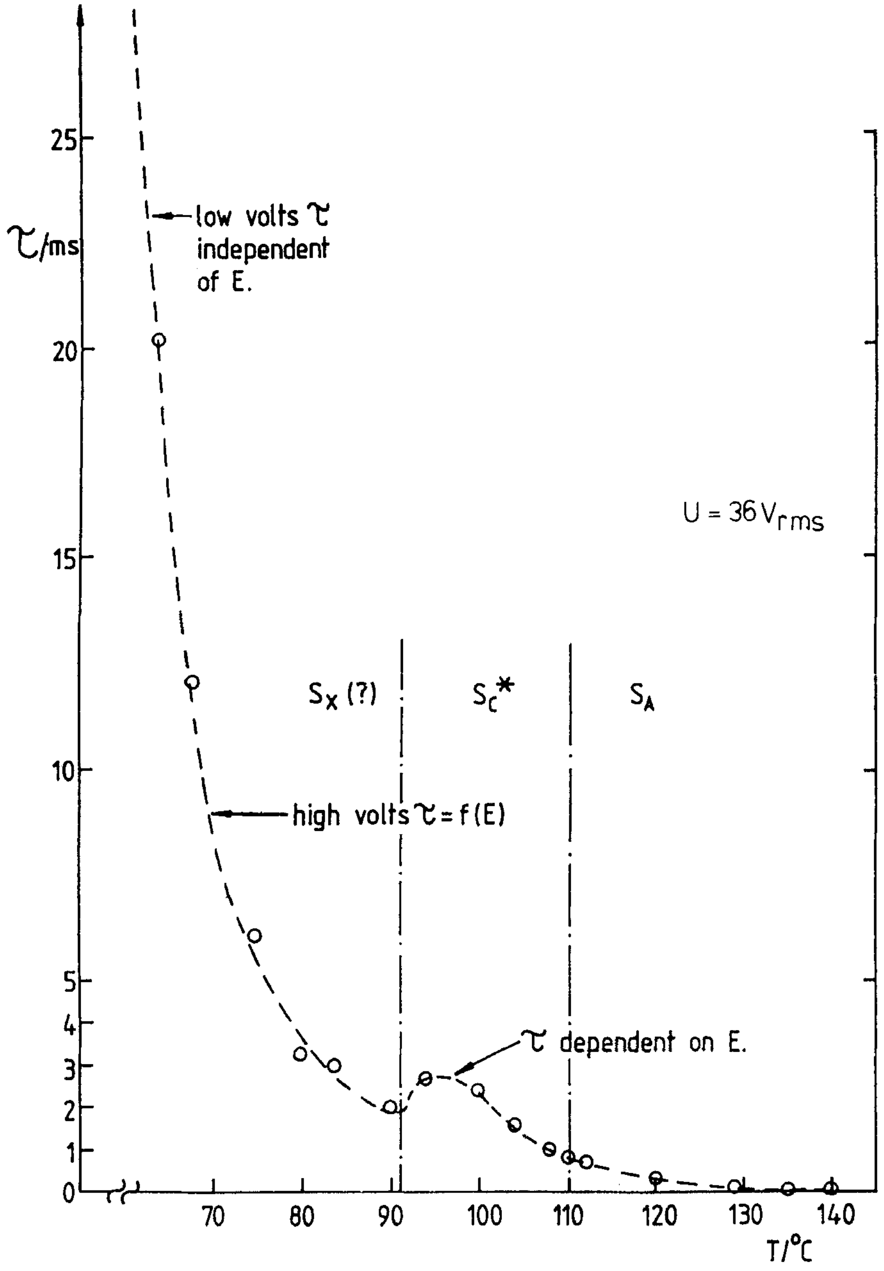

Figure 5. Copolymer (15 per cent): response time τ versus temperature (sample thickness 4 μm).

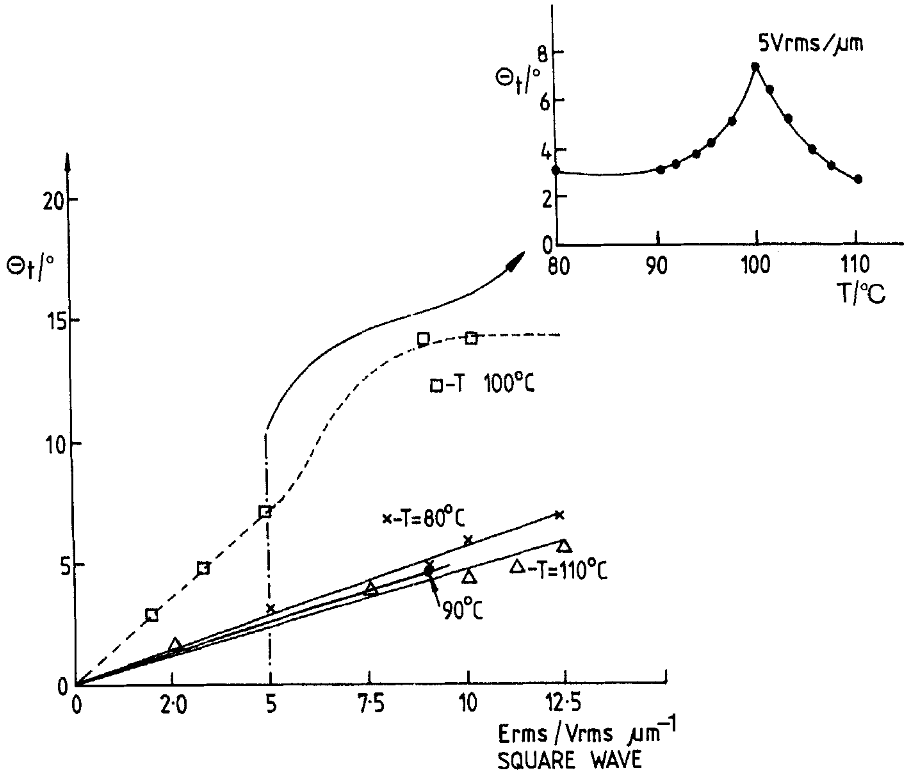

Figure 6. Copolymer (15 per cent): induced tilt angle θ_t as a function of applied field and temperature. The inset shows the variation of θ_t with temperature at a fixed field of 5 $V_{rms}/\mu m$.

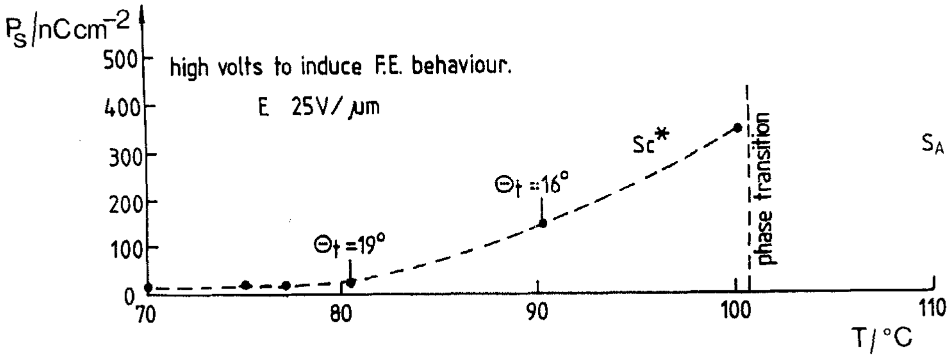

Figure 7. Copolymer (15 per cent): spontaneous polarization as a function of temperature. The plateau values of θ_t obtained for high fields are also given for comparison.

Table 2. Order parameter of the 5 per cent dye containing copolymer.

λ/nm	350	360
S	0·83	0·82

[11], recently discussed in low molar mass ferroelectric liquid crystals. Above the S_C^*–S_A transition the linear effect can be attributed to true electroclinic switching. We shall extend this discussion in a later paper where the electrooptic response of a number of similar ferroelectric liquid crystal polymers with different pitches will be discussed.

2.3. *Static order parameter*

Finally, we have measured the static orientational order parameters of the azo dye component of the copolymers (see table 2). Measurements were performed at room temperature in a frozen smectic phase in highly oriented samples (thickness 2 μm). Values of $S \geqslant 0{\cdot}82$ were recorded near to the absorption maxima at λ 350–360 nm. These data establish clearly that the guest dye moiety is well aligned, co-operatively, by the mesogenic host.

3. Experimental part

3.1. *Instrumental*

GPC: PL-gel with tetrahydrofuran as solvent and a polystyrene calibration. DSC: Perkin–Elmer DSC 2. Optical microscopy and tilt angle: microscope Jenapol, hot stage Linkam THM 600. Response time: 10–90 per cent, square wave electric field. Spontaneous polarization: Diamant bridge. Order parameter: Varian Cary 210 spectrophotometer. Parallel and crossed polarizers, measuring at room temperature using the homopolymer as reference. ^{1}H NMR: Bruker WM 400, $CDCl_3$. Elemental analysis: Perkin–Elmer 240C.

3.2. *4-[4-(10-Hydroxydecyloxy)-phenylazo]-ethylbenzoate*

7·4 mmol (2 g) of 4-(4-hydroxydecyloxy)-ethylbenzoate and 8 mmol (1·9 g) of 10-bromdecan-1-ol were dissolved in 15 ml of acetone, then 7·4 mmol (1 g) of K_2CO_3 and a pinch of KI were added. The reaction mixture was refluxed for two days. Chloroform (30 ml) was added and the undissolved material was filtered off. The chloroform solution was extracted twice with water, dried over $MgSO_4$ and evaporated. The product was recrystallized from acetone. Yield: 2·2 g (70 per cent); mp 103°C; ^{1}H NMR, $\delta = 1{\cdot}44$ t ($J = 7$ Hz, 3 H), 1·28–1·51 m (12 H), 1·57 quint ($J = 7$ Hz, 2 H), 1·82 quint ($J = 7$ Hz, 2 H), 3·64 t ($J = 7$ Hz, 2 H), 4·05 t ($J = 7$ Hz, 2 H), 4·41 quint ($J = 7$ Hz, 2 H), 7·11/7·90 AA'BB' ($J = 8{\cdot}5$ Hz, 4 H) 7·94/8·17 AA'BB' ($J = 8{\cdot}5$ Hz, 4 H).

3.3. *4-[4-(10-Acryloyloxydecyloxy)-phenylazo]-ethylbenzoat* II

4·7 mmol (2·0 g) of 4-[4-(10-hydroxydecyloxy)-phenylazo]-ethylbenzoate were dissolved in 15 ml of dry tetrahydrofuran and 5 mmol (0·7 ml) of triethylamine were added. 5 mmol (0·45 g) of acryloyl chloride were added dropwise at 60°C. The reaction mixture was cooled and stirred at room temperature for 16 h. The mixture was evaporated and 50 ml of methylene chloride were added. The methylene chloride solution was extracted with water, dried over $MgSO_4$ and evaporated. The solid residue was purified using F.C. on silica-gel with methylene chloride/petroleum ether (2/1) as eluent. Yield: 2·0 g

(89 per cent); mp 76°C; UV, $\lambda_{max} = 360$ nm ($CHCl_3$); ^1H NMR, $\delta = 1{\cdot}30$–$1{\cdot}52$ m (12 H), 1·43 t ($J = 7$ Hz, 3 H), 1·67 quint ($J = 7$ Hz, 2 H), 1·82 quint ($J = 7$ Hz, 2 H), 4·05 t ($J = 7$ Hz, 2 H), 4·15 t ($J = 7$ Hz, 2 H), 4·41 quint ($J = 7$ Hz, 2 H), 5·81 dd ($J = 10{\cdot}5/1{\cdot}5$ Hz, 1 H), 6·12 dd ($J = 17/10{\cdot}5$ Hz, 1 H), 6·40 dd ($J = 17/1{\cdot}5$ Hz, 1 H), 7·01/7·90 AA′BB′ ($J = 8{\cdot}5$ Hz, 4 H), 7·94/8·17 AA′BB′ ($J = 8{\cdot}5$ Hz, 4 H); elemental analysis: calc. C 69·96 per cent, H 7·56 per cent, N 5·83 per cent; found C 70·00 per cent, H 7·60 per cent, N 5·99 per cent.

3.4. *Synthesis of the polymers*

About 500 mg of a monomer mixture of the two monomers was dissolved in 4 ml of toluene. The solution was degassed by passing nitrogen for 15 min. AIBN (1 mol%) was added and the solution was degassed for another 5 min and polymerized at 70°C for 42 h. The (co)polymers were precipitated in cold methanol, redissolved in methylene chloride and reprecipitated. The polymers were purified using F.C. on silica-gel with methylene chloride/petroleum ether (1/1), then methylene chloride as eluents. The purified polymers were dried under reduced pressure. The composition of the copolymers was detected by UV spectroscopy. Yield: homopolymer 24 per cent, copolymer (5 wt% azocompound) 20 per cent, copolymer (15 wt% azocompound) 13 per cent.

Electrooptic properties were measured with 4 μm cells (rubbed polyimid layer). The polymers were oriented during filling the cells by capillary forces.

4. Conclusions

We have established that dyed copolymer ferroelectric materials may be synthesized and that these materials show interesting electrooptic switching phenomena. Both linear (electroclinic or deformed helix-like) and ferroelectric switching have been observed. At low fields ($\leqslant 5\,V_{rms}/\mu m$) the electrooptic response follows the applied field in a linear fashion over a very wide temperature range (~60°C to 140°C). Electroclinic coefficients of ~1–2 ($^\circ\mu m/V_{rms}$) were recorded and induced tilt angles ~10° were achieved. At high field strengths ($\sim 25\,V_{rms}/\mu m$) true ferroelectric switching was observed for the 15 per cent copolymer between ~70°C and ~105°C in the S_C^* phase. Above the S_C^*–S_A transition only true electroclinic switching was observed. At lower temperatures, i.e. in the S_C^* phase where both types of switching were observed, optical microscopy suggested a phase transition at ~90°C, the so-called S_X–S_C^* transition. The data suggest that this temperature marks an optical texture change due to a sharp change in the ferroelectric helix pitch and that the material remains in the S_C^* phase down to 60°C. High order parameters of about 0·82 were established for the dye moiety. Thus we conclude that dye ferroelectric materials have interesting electrooptic properties and that with suitable modifications to the chemical structures and/or blending in other materials it should be possible to reduce the phase transitions further. This opens the way to device applications involving fast modulators as well as display devices.

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