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Dielectric and electro-optical properties of ferroelectric side-chain liquid-crystalline polysiloxanes containing 4′-(2-chloro-3-methylpentanoyloxy)-4-alkanyloxybiphenyl side groups

Ging-Ho Hsiue* and Rong-Ho Lee
Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan 300, ROC

and Jenn-Chiu Hwang
Department of Chemical Engineering, Yuan-Ze Institute of Technology, Taoyuan, Taiwan 320, ROC
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A series of ferroelectric liquid-crystalline polymers (FLCPs) with siloxane backbone were synthesized in this study. The dynamics of these polymers was studied by broad-band dielectric spectroscopy (10^{-1} to 10^{7} Hz). The collective (Goldstone and soft mode) and molecular (α, β, γ, δ relaxation) relaxation processes were observed. These FLCPs exhibited large values of spontaneous polarization (larger than 190 nC cm^{-2}), fast switching time (less than 1 ms) and reversible bistable effects in the chiral smectic C (SmC*) phase.

(Keywords: ferroelectric LCP; polysiloxanes; relaxation processes)

INTRODUCTION

Low-molecular-weight liquid crystals with SmC* phase have been widely studied because of their ferroelectric properties, fast switching times and memory effect towards an applied electric field[1–3]. These characteristics make them particularly suitable for electro-optical applications, e.g. display and light valve devices. However, some difficulties are still encountered in controlling the orientation of molecules and uniform cell thickness for gaining a good memory effect. In order to overcome these difficulties, Shibaev *et al.*[4] polymerized ferroelectric liquid crystals (FLCs) in 1984. In that investigation, ferroelectric liquid-crystalline polymers (FLCPs) exhibited the desirable mechanical properties of polymers and the electro-optical properties of a low-molecular-weight FLC. This type of polymer, possessing high-speed response and memory effect, has recently attracted much attention[5–8]. Thoroughly understanding the thermal behaviour of FLCPs requires investigating molecular dynamics. Dielectric relaxation measurements are a suitable approach for undertaking such an investigation.

The molecular dynamics of LCPs have been studied extensively[9–12]. A complete nomenclature was introduced for the relaxation motions by Zentel *et al.*[9]. They investigated a series of liquid-crystalline polyacrylates and observed five different relaxation processes in these polymers. Three of the relaxation processes are the reorientations of the dipoles located at the centre of the mesogenic group (β relaxation), the end of the spacer group and the end-group below the glass transition temperature (T_g). The latter two are γ relaxations. At T_g, the centres of gravity of the mesogenic groups and the polymer main chain become mobile; dipole reorientations associated with this motion result in the α relaxation. The δ relaxation is the reorientation of the long axis of the mesogenic groups. This relaxation can be observed at higher temperatures than the T_g of the LCP. Other types of LCPs have also been investigated for their dielectric relaxation by several investigators[13,14].

The collective relaxations (Goldstone and soft mode) in a low-molecular-weight FLC with SmC* phase have been studied by several investigators[15–18]. The Goldstone mode appears in the SmC* phase because of the phase fluctuation in the azimuthal orientation of the director. The soft mode appears in the neighbourhood of the SmA–SmC* transition point, corresponding to the fluctuation of the tilt angle. In general, the soft mode is covered by the Goldstone mode owing to the greater relaxational strength of the Goldstone mode[18]. In the SmA phase, i.e. close to the phase transition temperature from the SmA phase to the SmC* phase ($T_{\mathrm{SmA-SmC*}}$), the occurrence of the soft mode seems to increase the dielectric constant. In the SmC* phase, the occurrence of the Goldstone mode enhances the dielectric constant

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* To whom correspondence should be addressed

markedly. These two relaxation modes are also observed for FLCPs[19,20]. They are important dielectric characteristics in the SmA and SmC* phases.

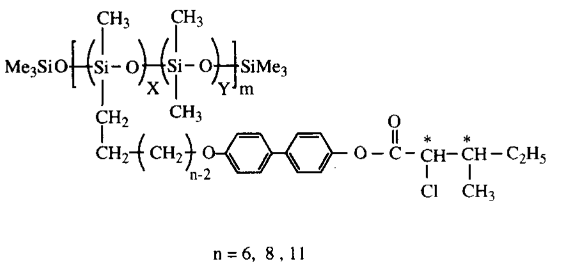
In this study, the molecular dynamics of a series of side-chain liquid-crystalline polysiloxanes was studied by dielectric spectroscopy. The spontaneous polarization, optical switching time and bistable effects of these side-chain liquid-crystalline polysiloxanes were also reported.

EXPERIMENTAL

The chemical structures of side-chain LCPs are shown in *Figure 1*. The LCPs contain a biphenyl unit and two chiral centres in the mesogenic group. They were prepared in the same manner as described in previous literature[21]. All of the products were purified by column chromatography using silica gel, and then recrystallized. A Seiko SSC 5200 differential scanning calorimeter was used to determine the thermal transitions. The thermal transitions were read at their maximum endothermic or exothermic peaks. Glass transition temperatures were read at the middle transition of the change in heat capacity. Heating and cooling rates were 5°C min^{-1} in all of these cases. Moreover, the transition temperatures were obtained from the specified second heating and cooling scans. A Nikon Microphoto-Fx polarized optical microscope equipped with a Mettler FP 82 hot stage was then used to observe the thermal transitions and to analyse the anisotropic textures. The heating/cooling rates for p.o.m. was 1°C min^{-1}. The temperature was controlled with an accuracy of ±0.1°C.

A dielectric spectroscope of Novocontrol GmbH was used in this study. A Schlumberger SI 1260 impedance/gain-phase analyser (frequency 10^{-1} to 10^7 Hz) and a Quatro temperature controller were used in this measurement. The measurement system is fully computer-controlled. A nitrogen gas heating system ranging from −170 to 300°C was used. The stability of the temperature adjustment was ±0.05°C. The LCP samples were sandwiched between two parallel metal electrode plates with a spacer of 50 μm.

The electro-optical measurements were taken using commercially available LC cells (EHC, Japan; 2 and 4 μm). The cells were filled with FLCP in the isotropic phase on a home-made hot bench by capillary forces. Good planar alignment was achieved by cooling the sample from the isotropic to the SmC* phase with a slow cooling rate (0.05°C min^{-1}). In the cooling scan, an electric field was also applied to the cell to aid the alignment of the LC molecules. The spontaneous polarization and switching times were measured by the triangular wave and electric field reversal method, respectively[22,23]. The bistable effects were determined with a photodiode measuring the transmitted light (He–Ne laser light: 632.8 nm) of the LCP sample placed between crossed polarizers when applying a square-wave voltage. Change of the transmission light intensity through the cell was recorded by a digital storage oscilloscope (Hitachi VC-6025).



X : Y = 100 : 0 (m = 80) 6P100, 8P100, 11P100
X : Y = 50 : 50 (m = 15) 8P50, 11P50

Figure 1 Chemical structures of side-chain FLCPs 6P100–11P50

RESULTS AND DISCUSSION

The thermal transitions and thermodynamic parameters of LCPs (6P100–11P50) are summarized in *Table 1*. The transition temperatures on the cooling scan are almost identical to the heating scan except for a very small supercooling (less than 7°C). The thermal transition temperature ranges of $T_{\text{I-SmA}}$, $T_{\text{SmA-SmC*}}$ and $T_{\text{SmC*-K}}$ are approximately 10, 4, and 10°C, respectively. LCP 6P100 showed an enantiotropic SmA phase; however, no SmC* phase was observed. Other LCPs exhibited SmA and SmC* phases in both heating and cooling states. Those results indicated that the SmC* phases of FLCPs 8P50 and 11P50 were narrower than that of FLCPs 8P100 and 11P100, respectively. This finding would suggest that the decrease of the mesogenic group content seems to reduce the thermal stability of the SmC* phase. The clearing temperature increases with an increase in the spacer length for all LCPs owing to the fact that the phase thermal stability increased with an increase in the spacer length. Similar results have also been reported by Richard *et al.*[24]. Simultaneously, the T_g decreased with an increase in the spacer length because of the plasticizing effect of long spacers. In addition, the phase transition temperatures of copolymers were lower than homopolymers because of the dilution of the mesogenic group on the polymer backbone[25]

The temperature and frequency dependence of the dielectric constant for LCPs 6P100, 8P100 and 11P100 are shown in *Figure 2*. Below the clearing temperature, the δ and α relaxations appeared separately in the SmA phase for LCP 6P100 (*Figure 2a*). The dielectric constant of LCP 6P100 increased slightly when these two relaxations occurred. For FLCPs 8P100 and 11P100,

Table 1 Phase transitions (°C) and phase transition enthalpies (mJ mg^{-1}) for polymers 6P100–11P50

Polymer	Phase transitions (corresponding enthalpy change) heating scan cooling scan
6P100	G 39.5 SmA 96(5.8) I I 98.9(4.8) SmA38.1(1.7) K
8P100	G 13.2 K 56.5(2.9) SmC* 101(0.8) SmA 131(5.7) I I 128.6(4.8) SmA99(0.9) SmC* 53(3.1) K
8P50	G −4.6 K 37.5(4.5) SmC* 58.5(0.2) SmA 81.5(6.4) I I 80.2(7.0) SmA 57.7(0.1) SmC* 33.3(4.4) K
11P100	G 6.7 K 67(7.3) SmC* 89.8(0.1) SmA 153.5(10.6) I I 150(8.4) SmA 85.8(0.1) SmC* 60(7.1) K
11P50	K 32 SmC* 40 SmA 100(10) I I 95(8) SmA 36.3 SmC* 27 K

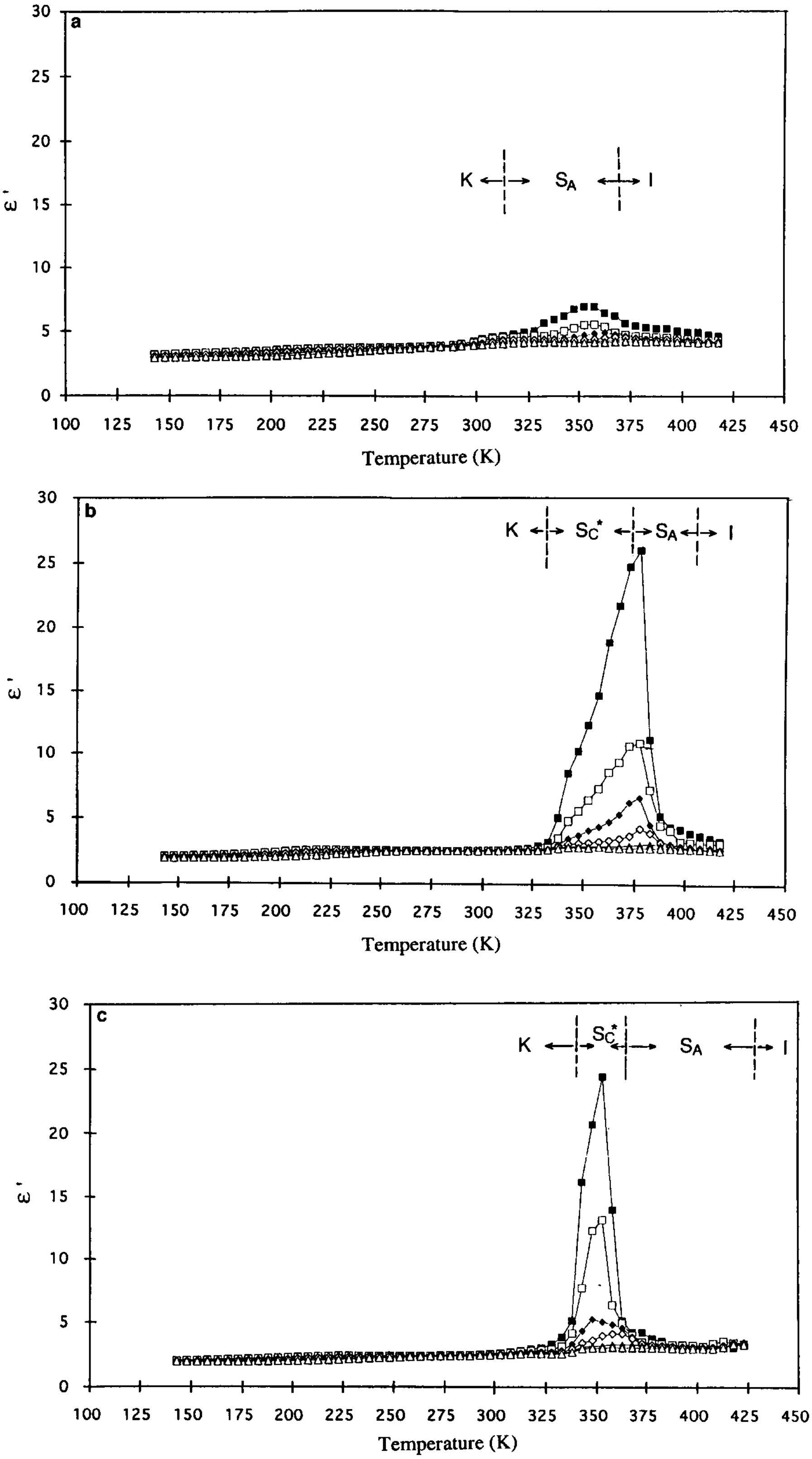


Figure 2 Temperature dependence of the dielectric constant (ε') at 1 (■), 10 (□), 10^2 (◆), 10^3 (◇), 10^4 (▲) and 10^5 Hz (△) for FLCPs 6P100 (a), 8P100 (b) and 11P100 (c), respectively. (The phase transition temperatures were determined by d.s.c.)

the dielectric constant increased sharply at the SmA–SmC* phase transition region due to the occurrence of the Goldstone and soft mode relaxations (*Figures 2b* and *2c*). The maximum value of the dielectric constant was observed near the SmA–SmC* phase. As the temperature decreased, the dielectric constant decreased, corresponding to the increase of the tilt angle in the SmC* phase. The molecules have such a large tilt angle that their rotational freedom is decreased somewhat by steric hindrance[26]. This would result in the decrease of molecular motion (Goldstone mode). In addition, the dielectric constant of FLCP 11P100 decreased more quickly than FLCP 8P100 in SmC* phase owing to the fact that the temperature range of SmC* phase for FLCP 11P100 was narrower than FLCP 8P100. The dielectric constant decreased markedly as the temperature decreased into the crystal phase for FLCP11P100. When the temperature decreased further, a smaller dielectric constant was observed because the mesogenic groups could not reorient easily below T_g.

The temperature and frequency dependences of the dielectric loss for FLCPs 8P100 and 8P50 are shown in *Figure 3*. Below the clearing temperature, the δ relaxation was not observed in the SmA and SmC* phases because of overlapping with the Goldstone and soft modes for both FLCPs. As the temperature decreased, the α, β and γ relaxations were observed for FLCP 8P50. The β relaxation was not observed between the α and γ relaxations of FLCP 8P100. Two factors are responsible for this occurrence. First, the orientation of the mesogenic groups and the layer structure for the SmC* phase were preserved as the temperature was reduced. Hence, the micro-Brownian motion was restricted by the interaction between the mesogenic groups[9]. Because of this, the β relaxation of FLCP 8P100 was not observed clearly. Secondly, the dilution of the mesogenic group on the polymer backbone would decrease the interaction between the mesogenic groups. Consequently, the β relaxation of FLCP 8P50 became more obvious.

The study of the dielectric behaviour of LCPs by the Cole–Cole plot (ϵ'' *versus* ϵ') is a common practice[9,10]. The Cole–Cole plot provides valuable information with regard to the dielectric relaxation process. Almost semicircular Cole–Cole plots at various temperatures are shown in *Figure 4* for the γ relaxation of FLCP 8P50. The relaxation strength (diameter of the circle) increased with increasing temperature. The centres of the circles were shifted along the ϵ' axis to larger ϵ' values at higher temperatures. In addition, complete Cole–Cole plots could not be obtained for the other relaxations owing to the fact that the relaxation frequency was shifted to a lower frequency range (below 0.1 Hz), and the Goldstone mode overlapped with δ relaxation. An Arrhenius plot of $\log(f_{\max})$ *versus* $1/T$ of the γ relaxation for FLCP 8P50 is shown in *Figure 5*. In that figure, the frequency at which ϵ'' reached a maximum ($f_{\max}$) was determined in the Cole–Cole plot. The activation energy of the relaxation was about $\Delta H = 37 \pm 4 \mathrm{mol}^{-1}$. The activation energy of

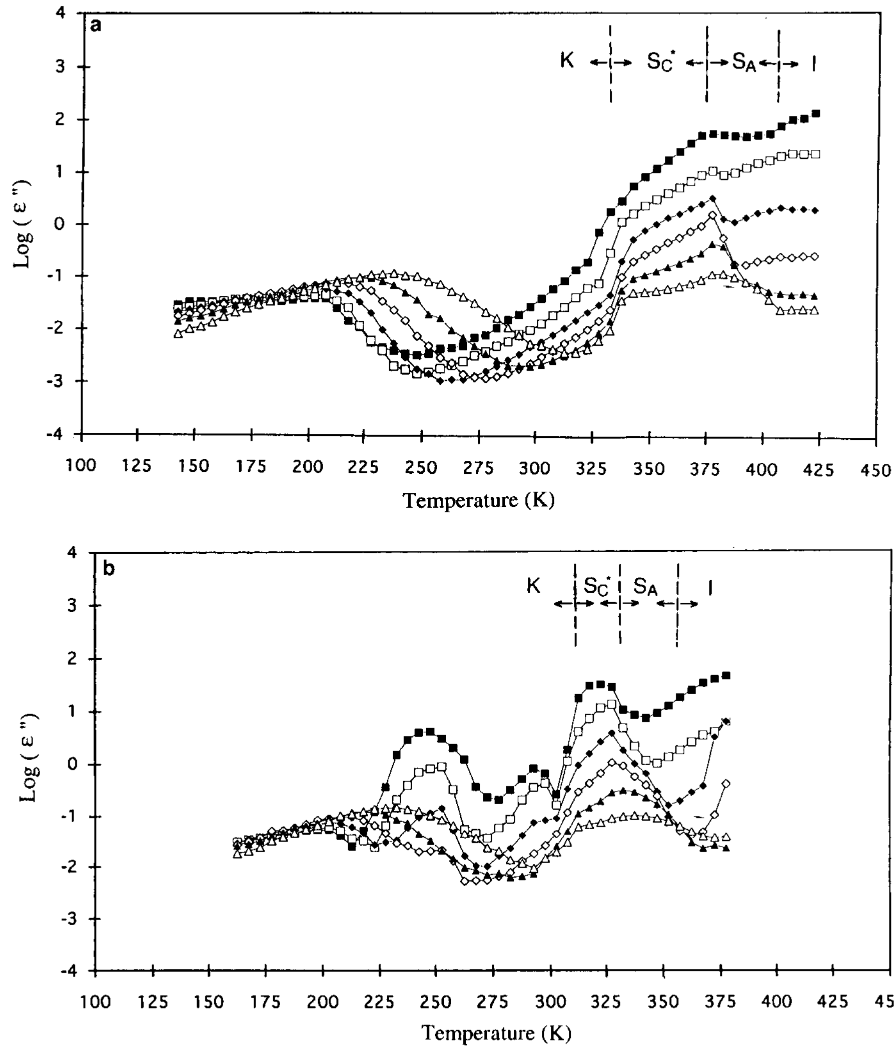


Figure 3 Temperature dependence of the dielectric loss ($\log \epsilon''$) at 1 (■), 10 (□), 10^2 (◆), 10^3 (◇), 10^4 (▲) and 10^5 Hz (△) for FLCPs 8P100 (a) and 8P50 (b), respectively. (The phase transition temperatures were determined by d.s.c.)

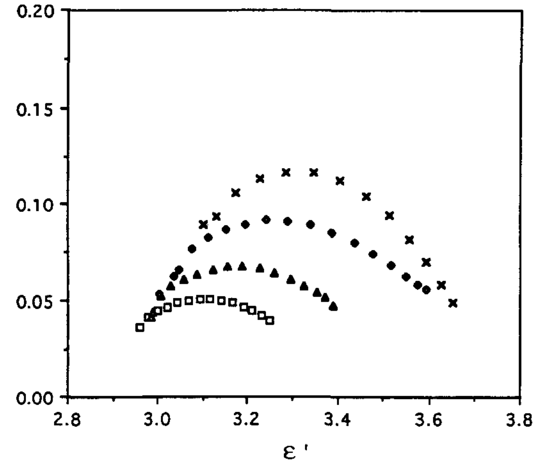


Figure 4 Cole–Cole plot of γ relaxation for FLCP 8P50 at different temperatures: 183 K (□), 193 K (▲), 203 K (◆) and 213 K (×)

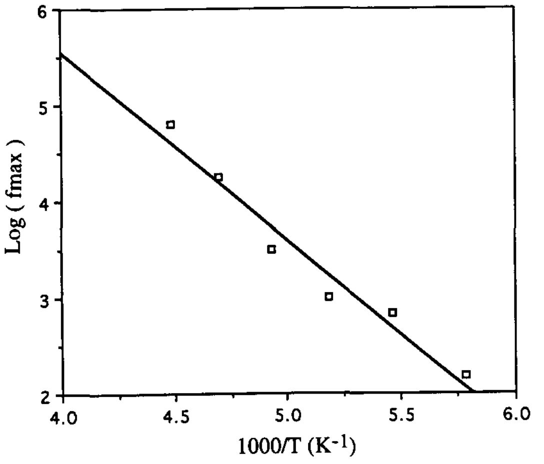


Figure 5 Temperature dependence of the relaxation frequency for the γ relaxation of FLCP 8P50

the γ relaxation for FLCP 8P50 is similar to literature values[9,10].

Figure 6 shows the polarization current peaks in a typical oscilloscope trace by applying a triangular wave voltage for the FLCP 8P100 at 96°C. The spontaneous polarization (P_s) at this temperature is 85 nC cm^{-2}. The temperature dependences of P_s for FLCPs 8P100 and 8P50 are shown in *Figure 7*. Large P_s values were observed for both FLCPs. The P_s increased with decreasing temperature in the SmC* phase for both FLCPs. The largest P_s values of the FLCPs 8P100 and 8P50 were 198 nC cm^{-2} at 80°C and 162 nC cm^{-2} at 43°C, respectively. The FLCP 8P100 have a larger P_s than FLCP 8P50, implying that a decrease in the mesogenic group content would reduce the P_s of FLCP. Moreover, the P_s decreased rapidly at a lower temperature range for both FLCPs. This phenomenon was initially observed by Uchida *et al.*[27] and subsequently studied in great detail by Gleeson[28]. This may be due to the fact that the molecules have a larger tilt angle at lower temperatures. As a result, the molecules could not be switched by the applied electric field. Another possible cause is increase of the viscosity, which leads to an imperfect reorientation of parts of the sample[29].

The electro-optical switching times were determined by the field reversal method[22,23]. The current response of the FLCP 8P100 by an applied square-wave voltage at 84°C is shown in *Figure 8*. The switching time τ was defined as the full width at half-maximum of the polarization current peak[23]. The switching time at this temperature is 6.5 ms. The switching times are shown in *Figure 9* as a function of temperature for the FLCPs 8P100 and 8P50. The switching time increased with a decrease in temperature for both FLCPs because of the increase of rotational viscosity and the decrease in the molecular mobility (at a tight pitch). In addition, the FLCP 8P50 have a faster switching time than FLCP 8P100 in the SmC* phase. A decrease in the mesogenic group content would result in a decrease of the viscosity and switching time for FLCP 8P50. For both FLCPs, the switching times were less than a millisecond at temperatures close to the SmC*–SmA transition.

The electro-optical effect of FLCP 8P50 was studied by applying a square-wave voltage across a thin cell. In this thin cell (2 μm), the helical structure of the SmC* phase was unwound by the application of an electric field and surface interactions. The energy required to unwind the helical structure decreases with the sample thickness,

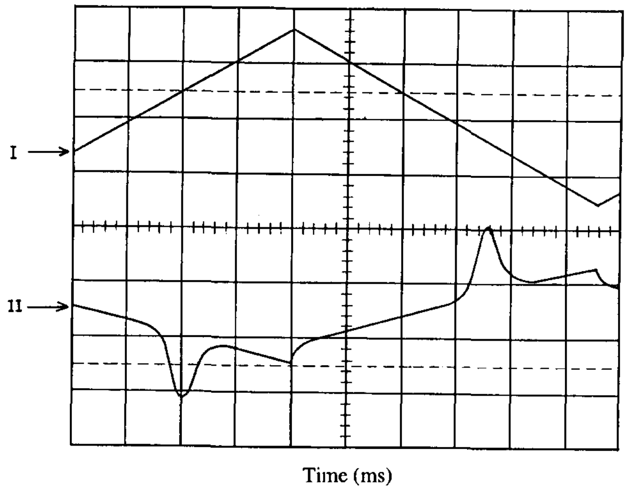


Figure 6 Oscilloscope trace of the ferroelectric swithing of FLCP 8P100 in a 4 μm cell at 96°C: (I) applied triangular-wave voltage 60 V_{rms}, $f = 4.5$ Hz; (II) current response as the voltage applied $P_s = 85$ nC/cm^{-2}, 10 ms/div

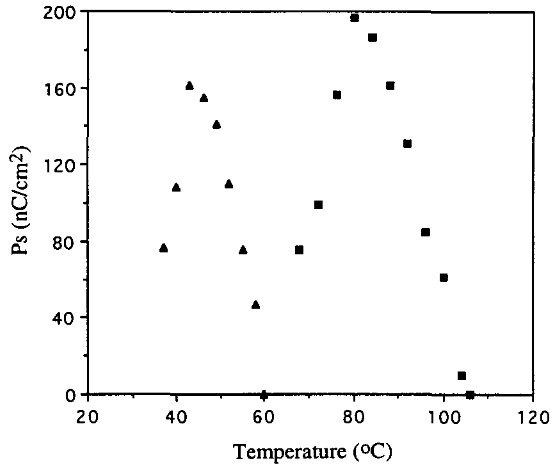


Figure 7 Temperature dependence of P_s for FLCPs 8P100 (■) and 8P50 (▲) (4 μm, 60 V_{rms}, 4.5 Hz)

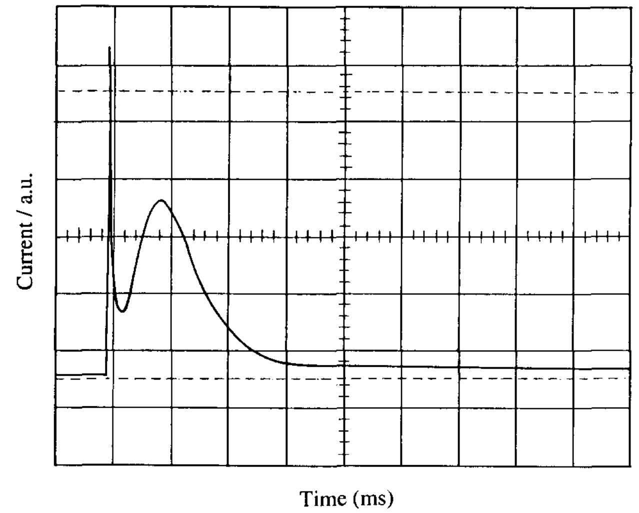


Figure 8 Current response as a function of time for FLCP 8P100 in a 4 μm cell at 84°C (applied square-wave voltage 60 V_{rms}, $f = 4.5$ Hz, $\tau = 6.5$ ms, 5 ms/div)

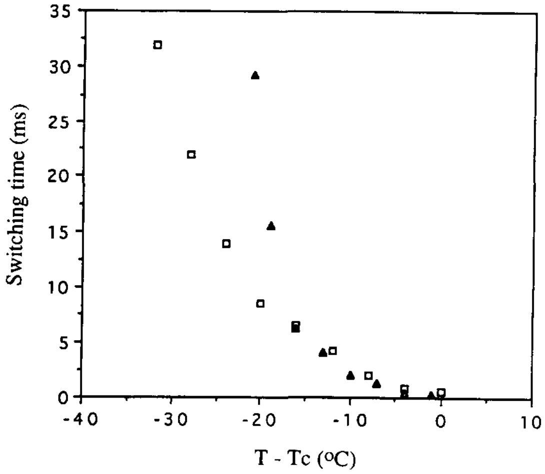


Figure 9 Temperature dependence of the switching time for FLCPs 8P100 (□) and 8P50 (▲) (4 μm, 60 V_{rms}, 4.5 Hz, $T_c = T_{SmA\text{-}SmC^*}$)

and complete unwinding of the helical structure occurs in a sufficiently thin sample. This thin cell thickness is approximately of the order of or less than the pitch of the sample[22]. Therefore, the uniform alignment of the molecular long axis can be obtained. Moreover, the molecular director can be switched between two surface-stabilized states by applying an electric field across a thin sample. These two stable states were separated by an angular difference of twice the tilt angle. The FLCP 8P50 exhibited bistable and reversible light switching driven by an electric field. The applied electric field with positive and negative rectangular voltage pulses with adjustable time separation is shown in *Figure 10a*. Both optical switching states were maintained even after the field was turned off (memory effect). Those results are shown in *Figures 10b* and *10c*. The molecular director stabilized at each state for a period longer than 60 s after the applied pulse voltage was turned off. The FLCP exhibited excellent bistable and reversible light switching effects, thereby making them particularly suitable for electro-optical applications, e.g. memory and light valve devices[30].

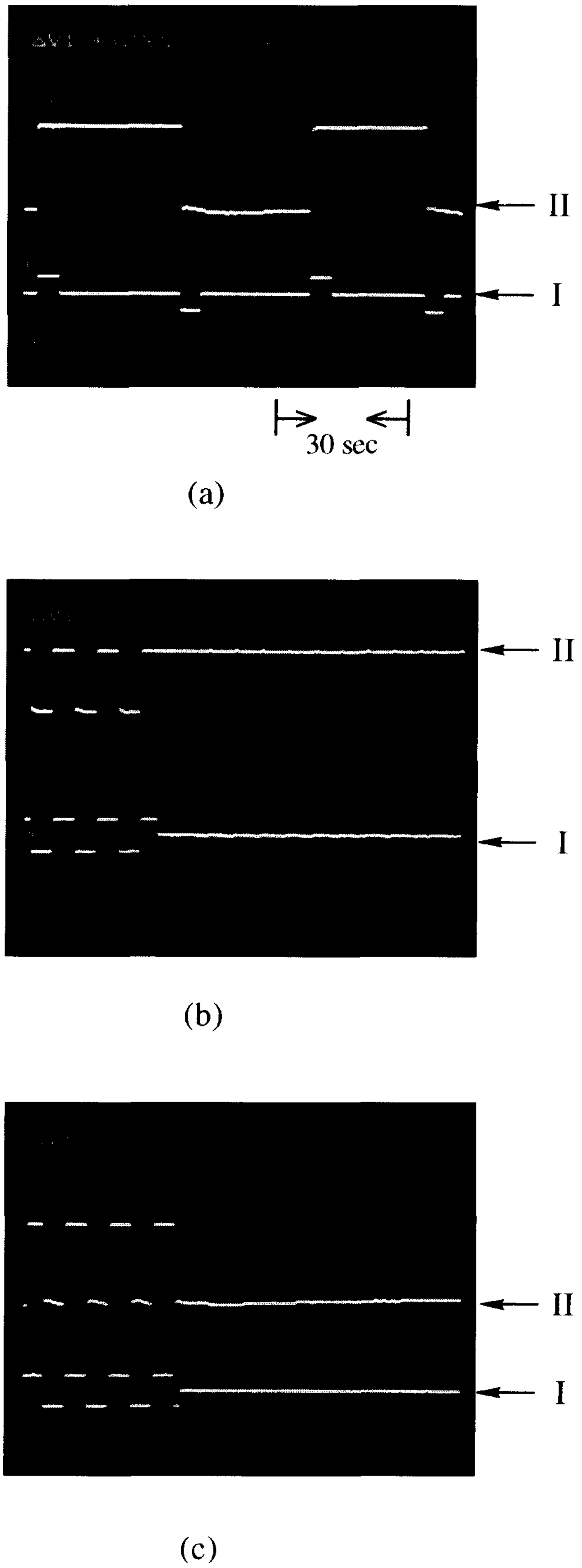


Figure 10 Oscilloscope traces for the intensity of light transmitted through a 2 μm cell of FLCP 8P50 at 49°C by applying a square-wave voltage: (a) light switching between two stable states; (b), (c) light transmission at up and down states, respectively. (I) Alternating positive and negative voltage ± 30 V_{rms}; (II) intensity of light transmission (a.u.)

CONCLUSION

Dielectric behaviour and electro-optical properties of a series of FLCPs with different contents of mesogenic groups were investigated in this work. The temperature range of SmC* phase and all of the transition temperatures decrease with a decrease in the content of the mesogenic groups. The collective and molecular relaxations of these FLCPs were also observed. The dielectric constant was enhanced markedly because of the occurrence of the Goldstone mode in the SmC* phase. The dilution of the mesogenic group on the polymer backbone would decrease the interaction between the mesogenic groups. Consequently, the β relaxation of FLCP became more obvious. The dilution of the mesogenic groups resulted in a decrease in the spontaneous polarization and switching time. In addition, the decrease in viscosity would favour the alignment of the mesogenic groups in a thin cell for FLCP. Furthermore, the bistable and reversible light switching effect was successfully achieved in the SmC* phase upon application of alternating positive and negative d.c. electric fields for FLCP 8P50. The bistable state was maintained (memory effect) even after the electric field was turned off. With the above properties, the FLCPs were suitable for electro-optical applications.

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