Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Fast switching ferroelectric side-chain liquid-crystalline polymer and copolymer

J. Naciri[a]; S. Pfeiffer[ab]; R. Shashidhar[ac]
[a] Center for Bio/Molecular Science and Engineering, Code 6090, Naval Research Laboratory, Washington, D.C., U.S.A. [b] Department of Chemistry, Georgetown University, Washington, D.C., U.S.A. [c] Also at Geo-Centers, Inc., 10904 Indian Head Highway, Fort Washington, U.S.A.

To cite this Article Naciri, J. , Pfeiffer, S. and Shashidhar, R.(1991) 'Fast switching ferroelectric side-chain liquid-crystalline polymer and copolymer', Liquid Crystals, 10: 4, 585 — 591

To link to this Article: DOI: 10.1080/02678299108036446

URL: http://dx.doi.org/10.1080/02678299108036446

LIQUID CRYSTALS, 1991, VOL. 10, NO. 4, 585–591

Fast switching ferroelectric side-chain liquid-crystalline polymer and copolymer

by J. NACIRI, S. PFEIFFER† and R. SHASHIDHAR*‡
Center for Bio/Molecular Science and Engineering, Code 6090,
Naval Research Laboratory, Washington, D.C. 20375-5000, U.S.A.

(*Received 16 May 1991; accepted 11 June 1991*)

New ferroelectric side-chain liquid-crystalline polymers, a copolymer and a homopolymer, with siloxane backbone and a triaromatic mesogen as the side group have been synthesized. The materials exhibit a chiral smectic C phase over a large temperature range extending to room temperature. They possess high values of spontaneous polarization: 105 nC cm^{-2} for the homopolymer and 180 nC cm^{-2} for the copolymer. The electro-optic switching time in the chiral smectic C phase is extremely fast (150 μs). In the smectic A phase, an electroclinic effect with switching times less than 100 μs and with field induced tilt angles of 18° is observed.

Since the discovery of ferroelectricity in liquid crystals [1] and the subsequent demonstration of the surface-stabilized ferroelectric liquid crystal device [2], there has been considerable activity aimed at synthesizing new, low molecular mass mesogens with a large value of spontaneous polarization (P_s) and a fast electro-optical response time (t). Can similar physical properties be achieved in side-chain ferroelectric liquid-crystalline polymers? Previous work on side-chain liquid-crystalline polymers exhibiting nematic phases showed that their switching times in the twisted nematic mode are two to three orders of magnitude larger than those of nematic monomers [3]. This increase can be attributed to the high viscosity of the polymers. The situation could, however, be very different in the chiral smectic C (S_C^*) phase of ferroelectric liquid-crystalline polymers. The molecular rotation constituting the ferroelectric switching in such polymers is the rotation of the mesogenic side group. This rotation is essentially a free rotation because the spacer groups effectively decouple the side groups from the polymer backbone. Hence the electro-optic response times of ferroelectric liquid-crystalline polymers could be similar to those of low molecular mass liquid crystals. There have been reports of the observation of the S_C^* phase in side-chain liquid-crystalline polymers [4–9]. Typically, the observed switching times of ferroelectric liquid-crystalline polymers have been in the millisecond regime [10, 11]. In this communication we report the synthesis of two new side-chain ferroelectric liquid-crystalline polymers (a copolymer 10PPB2-CO and a homopolymer 10PPB2-P) exhibiting broad S_C^* phases extending to room temperature, large polarizations and fast switching times in the S_C^* phase. We also report an electroclinic effect in the S_A phase of these new materials.

---

* Author for correspondence.

† Also at Department of Chemistry, Georgetown University, Washington, D.C., 20057, U.S.A.

‡ Also at Geo-Centers, Inc., 10904 Indian Head Highway, Fort Washington, MD20744, U.S.A.

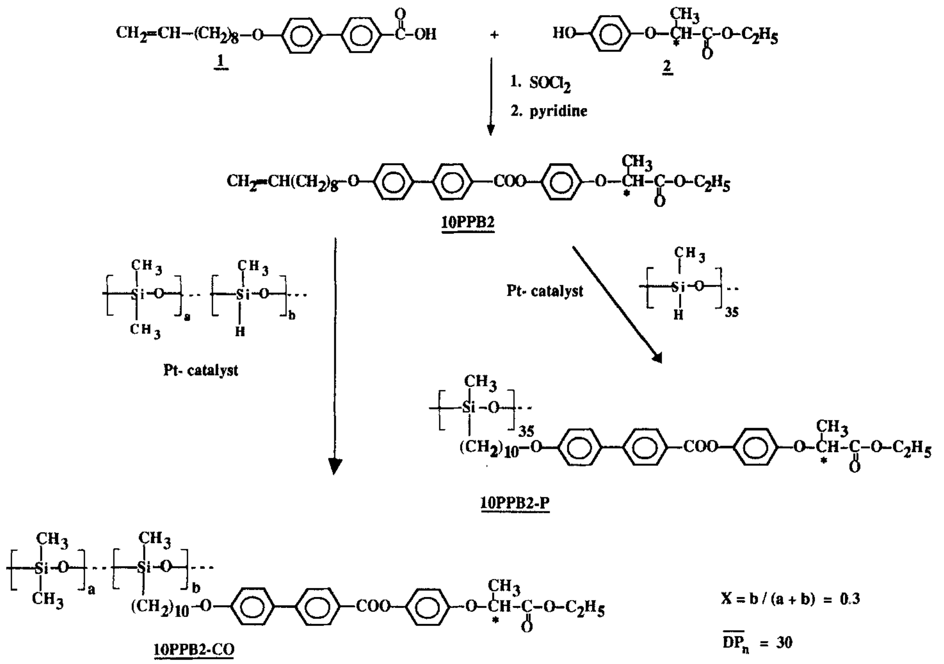
0267–8292/91 $3·00

The structures of the ferroelectric mesogen (*R*)-4′-(1-ethoxycarbonyl-1-ethoxy)phenyl-4-[4-(9-decenyloxy)-phenyl]benzoate 10PPB2, the homopolymer 10PPB2-P and the copolymer 10PPB2-CO are given in the scheme. 10PPB2 was synthesized by reaction of the acid chloride of **1** with **2** in the presence of pyridine. The sample was purified by silica gel chromatography, followed by recrystallization from ethanol. The molecular structure was confirmed by gas chromatography, IR, ^{1}H NMR and elemental analysis. The corresponding homopolymer (copolymer) was obtained through the classical hydrosilylation reaction [12, 13] between the olefinic derivative 10PPB2 and the poly(methylhydroxy-siloxane), its mean moleculer mass $\bar{M}_n$ being 2270 (poly[(30–35 per cent)methylsiloxane-co-(65–70 per cent)dimethylsiloxane], $\bar{M}_n = 2000$–2100). The polymers were purified by several precipitations from tetrahydrofuran solution into methanol. Details of the synthesis and the results of the analysis will be reported elsewhere.

The phases exhibited by the materials have been identified by optical microscopy while the phase transition temperatures were measured by differential scanning calorimetry (Perkin–Elmer DSC-7). The transition temperatures are given below:

10PPB2 (S_I^* or S_F^* 55·5°C) C 67·0°C S_C^* 95·4°C S_A 125·4°C I,
10PPB2-P g 25°C 58°C S_C^* 178°C S_A 215–222°C I,
10PPB2-CO g (not found) C 15°C S_C^* 136°C S_A 150–162°C I.

The temperature range of the S_C^* phase for the mesogen is about 40 K. This range is considerably enhanced for both the homopolymer and the copolymer; 120 K for the former and more than 121 K for the latter. Thus both the homopolymer and the copolymer exhibit, on cooling, the S_C^* phase over a wide temperature range extending to



The structures of the ferroelectric mesogen (*R*)-4′-(1-ethoxy-carbonyl-1-ethoxy)phenyl-4-[4-(9-decenyloxy)-phenyl]benzoate 10PPB2, the homopolymer 10PPB2-P and the copolymer 10PPB2-CO.

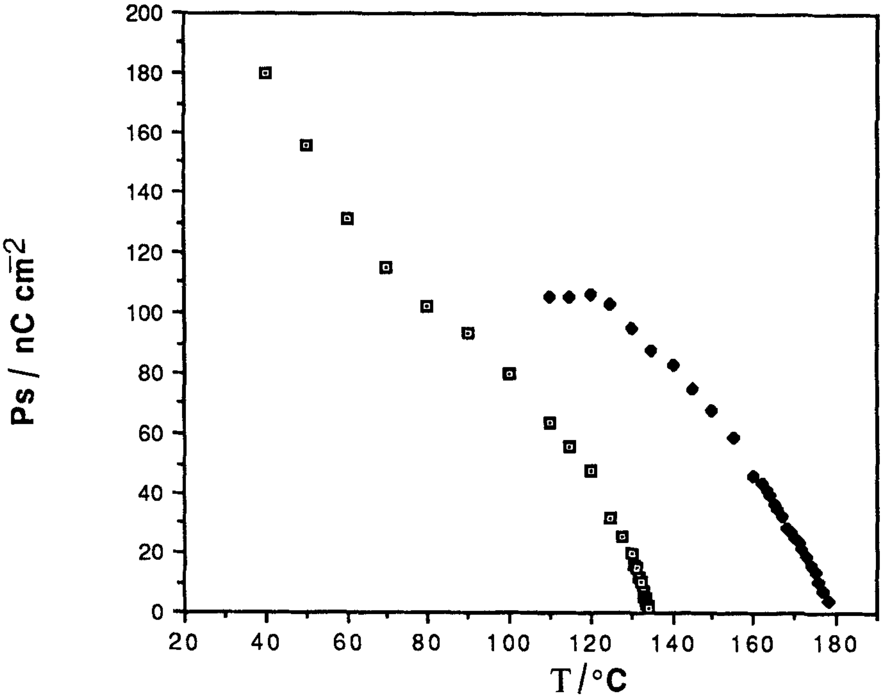


Figure 1. The temperature dependence of P_s for the homopolymer 10PPB2-P (◆) and the copolymer 10PPB2-CO (▣).

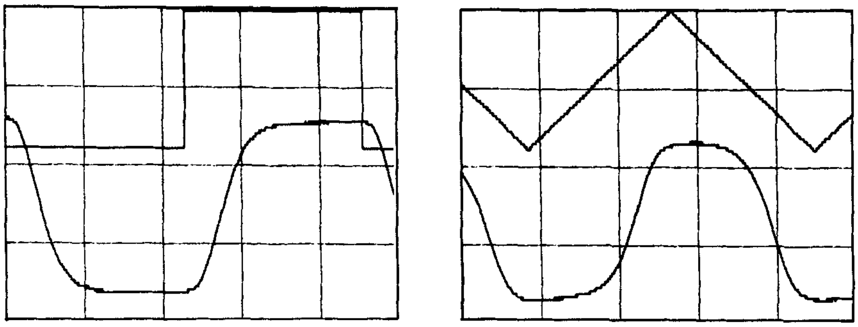

(*a*) (*b*)

Figure 2. Oscilloscope traces for the intensity of the light transmitted through a 15 μm sample of the copolymer 10PPB2-CO in its S_C^* phase at $T = 129°C$ on applying an AC voltage to the cell. (*a*) Square wave voltage ($f = 1{\cdot}1$ kHz, $U = \pm 100$ V, 0·2 ms per division and the switching time is 152 μs. (*b*) Triangular wave voltage ($f = 550$ Hz, $U = \pm 100$ V and 0·5 ms per division).

room temperature. In the case of the homopolymer, a partial crystallization appears to occur at about 50°C, the rest of the sample remaining in the S_C^* phase until T_g, the glass transition temperature.

The spontaneous polarization has been measured by the triangular wave method [14]. A 20 V amplitude triangular wave (frequency range 0·1 Hz to 100 Hz) was applied across a 4 μm thick sample and the current was determined by measuring the voltage drop across a reference resistance with a storage oscilloscope. The polarization current

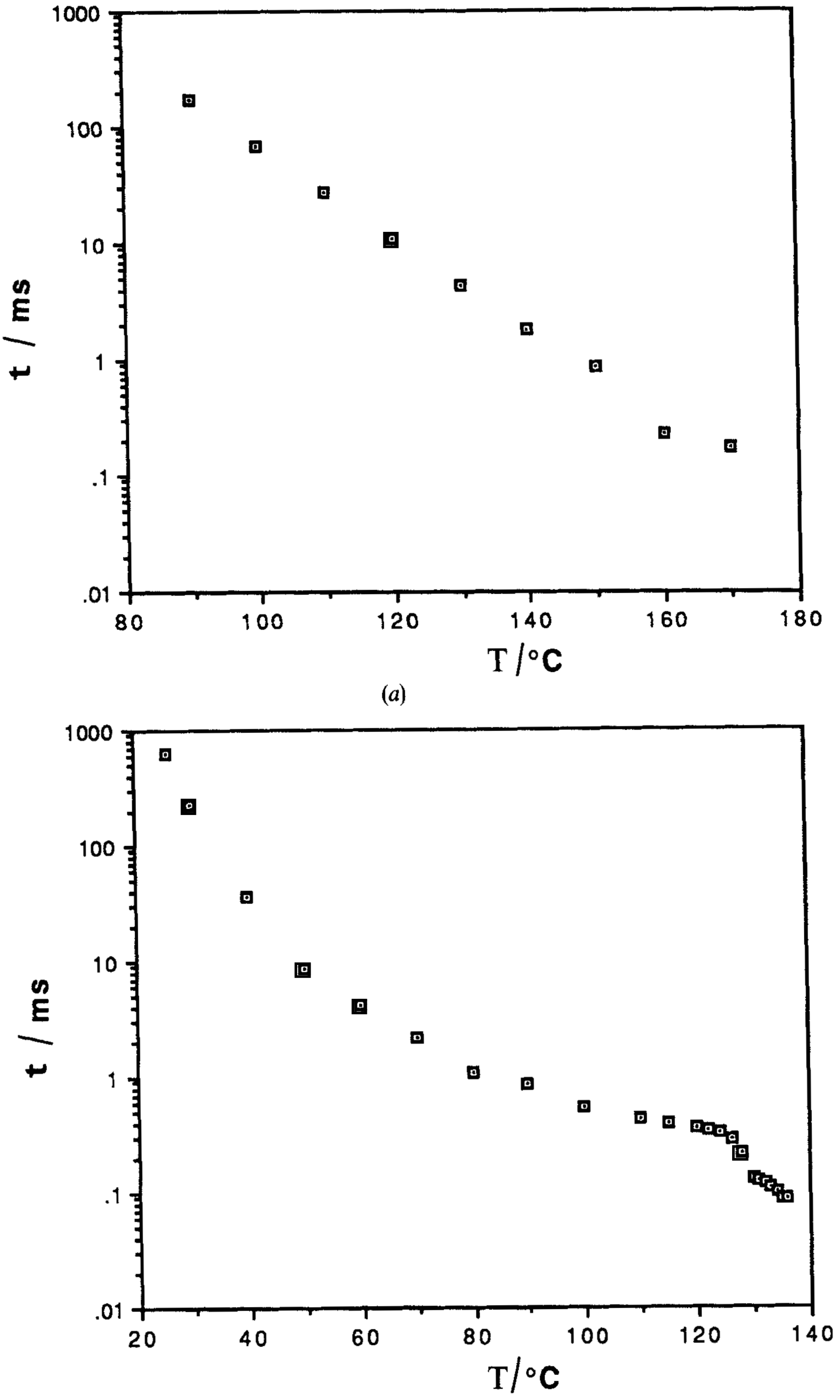


Figure 3. The temperature dependence of the switching times (t) in (a) the S_C^* phase of the polymer 10PPB2-P (10 μm cell, $U = \pm 34$ V) and (b) the S_A and S_C^* phases of the copolymer 10PPB2-CO (15 μm cell, $U = \pm 100$ V).

was separated from the ohmic and capacitive contributions and then integrated by a computer. The temperature dependence of the spontaneous polarization for the homopolymer as well as the copolymer is shown in figure 1. The highest P_s that we have measured for the copolymer is 180 nC cm^{-2} at 40°C while that for the homopolymer is 105 nC cm^{-2} at 110°C. No measurements could be made for the homopolymer below this temperature because of its large viscosity. At any given relative temperature $T - T_{S_C^*S_A}$, P_s has similar values for both the homopolymer and the copolymer. Also, in both cases, P_s goes continuously to zero at the S_C^*–S_A transition indicating the second order nature of the transition.

The electro-optic switching times were determined with a photo diode measuring the transmitted light of the sample placed between crossed polarizers. The switching time t is defined as the time required for an intensity change from 0 per cent to 90 per cent on applying a square wave. Typical oscilloscope traces showing the change in the optical transmission for the copolymer are shown in figure 2. It is clear that the S_C^* phase exhibits two stable states which can be addressed either by a square wave or a triangular wave. The response times for the triangular wave are about twice as large as those for the square wave. Plots of the switching time t versus temperature in the S_C^* phase for the homopolymer and the copolymer are given in figures 3 (*a*) and (*b*), respectively. For both polymers, the switching is very fast, switching speeds are less than a millisecond close to the S_C^*–S_A transition. Also, the copolymer exhibits a clear bistable switching, albeit slow ($t \approx 600$ ms) even at room temperature.

For both the homopolymer and the copolymer, a pronounced electroclinic effect in the S_A phase is observed. Figure 4 shows the oscilloscope traces corresponding to the optical transmission in the S_A phase of the copolymer. The optical signal follows the applied electric field. This switching process is different from the bistable switching seen in the S_C^* phase. The optical contrast observed on applying square waves of different amplitudes is approximately proportional to the applied field strength. The switching times also show a dependence on the magnitude of the electric field, but only close to the S_C^*–S_A transition. For instance, at $T - T_{S_C^*S_A} = 0{\cdot}5$ K the switching times if 73 μs for a voltage of 100 V, while it is 85 μs for 50 V applied across a 10 μm sample. On increasing the temperature, these differences diminish and for $T - T_{S_C^*S_A} > 5$ K, the switching times are independent of the electric field strength. The shortest electronic

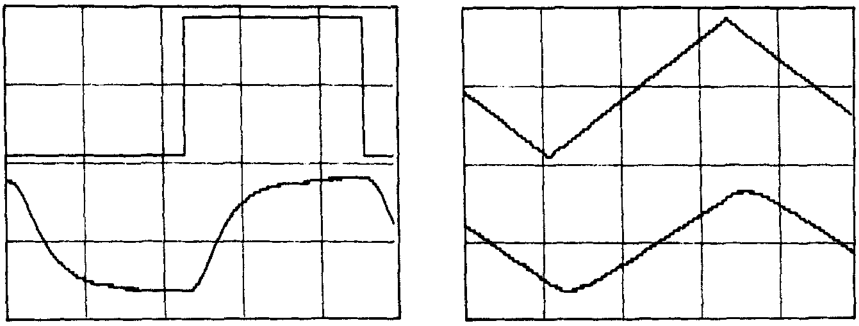

(*a*) (*b*)

Figure 4. Oscilloscope traces for the intensity of light transmitted through a 15 μm sample of the copolymer 10PPB2-CO in its S_A phase at 136°C on applying (*a*) square waves ($f = 2{\cdot}2$ kHz, $U = \pm 100$ V, 0·1 ms per division; the switching time is 94 μs) and (*b*) triangular waves ($f = 1{\cdot}1$ kHz, $U = \pm 100$ V, 0·2 ms/div)$^{-1}$.

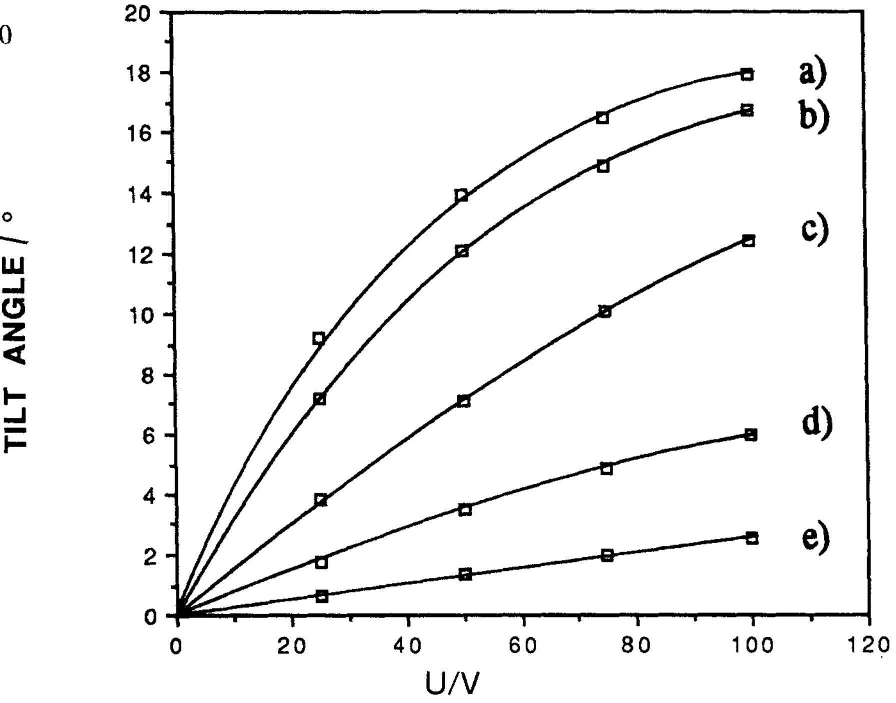


Figure 5. The voltage dependence of the electric field induced tilt angle at different temperatures $T - T_{S_C^*S_A}$ ((*a*) 0·5 K, (*b*) 1·0 K, (*c*) 2·5 K, (*d*) 5·0 K, (*e*) 10·0 K) in the S_A phase of the copolymer 10PPB2-CO in a 10 μm cell. The solid lines are guides to the eye.

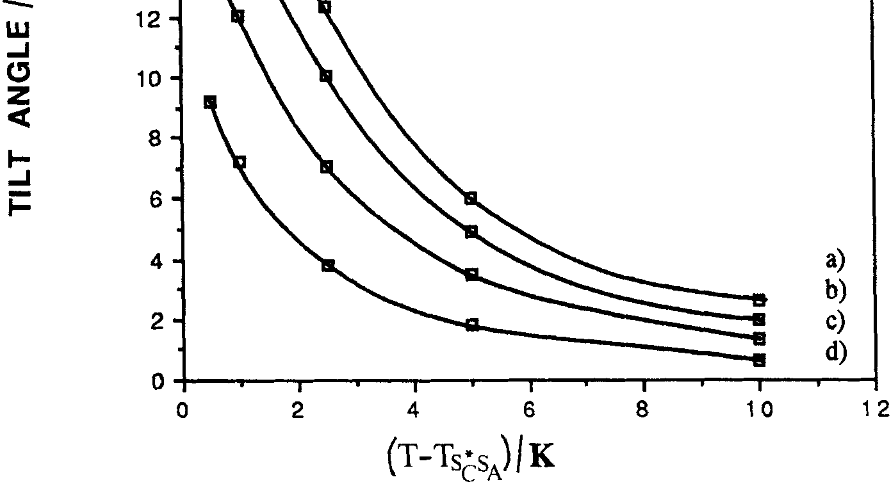


Figure 6. The temperature dependence of the electric field induced tilt angle at different voltages ((*a*) 100 V, (*b*) 75 V, (*c*) 50 V, (*d*) 25 V) in the S_A phase of the copolymer 10PPB2-CO. The solid lines are guides to the eye.

switching time observed for 10PPB2-CO is less than 30 μs at $T - T_{S_C^*S_A} = 10$ K. Similar results on the electroclinic switching have recently been obtained in other side-chain polymers [15, 16].

The dependence of the field induced tilt angle on the applied voltage is plotted in figure 5 for different temperatures in the S_A phase of 10PPB2-CO. The tilt angle exhibits a linear dependence for $T - T_{S_C^*S_A} > 2{\cdot}5$ K while for temperatures closer to the phase transition, the variation is slower. Figure 6 shows the temperature dependence of the induced tilt angle for different values of the applied voltage. Close to the S_C^*–S_A transition, a tilt angle of nearly 18° is induced for an applied voltage of 100 V across a 10 μm cell. The qualitative features of our electroclinic results agree with recent theoretical calculations [17].

In summary, the ferroelectric polymers 10PPB2-P and 10PPB2-CO are shown to exhibit the S_C^* phase with a large spontaneous polarization which is comparable with values for low molecular mass ferroelectric liquid crystals. They also have very short electro-optic switching times and hence are of considerable importance for applications. It would be of interest to see how the switching times and polarization values are affected by varying the spacer length between polymer backbone and mesogenic side group. Such investigations are underway.

We are extremely thankful to Drs Tom Fare, Patrick Keller, B. R. Ratna and Dave Stenger for many helpful discussions. J. N. acknowledges the support of the National Research Council and S. P. that of the Deutsche Forschungsgemeinschaft (Germany). Partial financial support from the Office of Naval Research is also gratefully acknowledged. Thanks are also due to Ms Shelley De Lozier for her technical editing.

References

[1] Meyer, R. B., Liebert, L., Strzelecki, L., and Keller, P., 1975, *J. Phys. Lett., Paris*, **36**, 69.
[2] Clark, N. A., and Lagerwall, S. T., 1980, *Appl. Phys. Lett.*, **36**, 899.
[3] Haws, C. M., Clark, M. G., and Attard, G. S., 1989, *Side Chain Liquid Crystal Polymers*, edited by C. B. McArdle (Blackie), p. 196.
[4] Shibaev, V. P., Kozlovskii, M. V., Beresnev, L. A., Blinov, L. M., and Plate, N. A., 1984, *Polym. Bull.*, **12**, 299.
[5] Decobert, G., Dubois, J. C., Esselin, S., and Noel, C., 1986, *Liq. Crystals*, **1**, 307.
[6] Zentel, R., Reckert, G., and Reck, B., 1987, *Liq. Crystals*, **2**, 83.
[7] Esselin, S., Bisio, L., and Noel, C., 1987, *Liq. Crystals*, **2**, 505.
[8] Parmar, D. S., Clark, N. A., Keller, P., Walba, D. M., and Wand, M. D., 1990, *J. Phys., Paris*, **51**, 355.
[9] Dumon, M., Nguyen, H. T., Mauzac, M., Destrade, C., Arachard, M. F., and Gasparoux, H., 1990, *Macromolecules*, **23**, 355.
[10] Scherowsky, G., Schliwa, A., Springer, J., Kühnpast, K., and Trapp, W., 1989, *Liq. Crystals*, **5**, 1281.
[11] Ushida, S., Morita, K., Miyoshi, K., Hashimoto, K., and Kawasaki, 1988, *Molec. Crystals liq. Crystals*, **155**, 95.
[12] Gibson, T., 1980, *J. org. Chem.*, **45**, 1095.
[13] Percec, V., and Hahn, B., 1989, *Macromolecules*, **22**, 1588.
[14] Miyasato, K., Abe, S., Takezoe, H., Fukada, A., and Kuze, E., 1983, *Jap. J. appl. Phys.*, **22**, L661.
[15] Flatichler, K., Keller, P., Komitov, L., and Skarp, K., 1990, *13th International Liquid Crystal Conference*, Vancouver, Poster POL-64-P.
[16] Bömelburg, J., Heppke, G., and Hoolidt, J., 1991, *20th Freiburger Arbeitstagung Flüssigkristalle*, Freiburg, Germany.
[17] Abdulhalim, I., and Moddel, G., 1991, *Liq. Crystals*, **9**, 493.