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Thermal surface switching and thermo electro-optical properties of nematic liquid crystals

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In liquid crystal technology, polymeric layers are used to obtain thermally stable planar or homeotropic alignments of nematic liquid crystals (NLC). Here we report a reversible temperature-induced switching with NLCs between these two alignments. The alignment, on a few copolymers, is homeotropic at low temperatures and planar at higher temperatures. The transition from homeotropic to planar occurs in a narrow temperature range. The transition temperature (T_{HP}) depends on the NLC for a given copolymer. The reduced transition temperatures (T_{NP}/T_{NI}), are correlated, for a selected copolymer, with the ratio (k_{33}/k_{11}) of the bend to splay elastic constants of NLCs. For a given NLC, the transition temperature (T_{HP}) can be shifted by the composition of the copolymer. By combining commercial NLC mixtures with an appropriate copolymer, we found transition temperatures T_{HP} in the range between $-30°C$ and $+120°C$. Experimental results on the surface switching of NLCs, with positive and negative dielectric anisotropies, on two copolymers are reported. A tentative explanation, based on a conformational change of the surface molecules in interaction with the NLC molecules, is presented.

1. Introduction

Liquid crystal displays (LCD) are among the most used and strongly developing display types. In these displays, switching is effected by an electrical field, from planar to homeotropic or the inverse, depending on the dielectric anisotropy of the NLC used. Thin organic layers are used to obtain an homogeneous planar or homeotropic alignment of the NLC molecules [1]. These layers ensure thermally constant alignments of NLCs, almost independently of their chemical composition. Recently two examples of thermally induced reversible transitions from homeotropic to planar alignment, near to the nematic–isotropic transition temperatures (T_{NI}), were described [2, 3]. Another case of a reversible alignment transition of a NLC is that induced by photochemical *cis–trans*-isomerization of azobenzene contained in the polymeric alignment layer [4].

Here we report a new type of thermally induced surface switching from a low temperature homeotropic to a higher temperature planar alignment of NLCs. The alignment layers are composed of perfluorocopolymers with homeotropic and planar aligning properties built in the same macromolecule.

Experimental results obtained with various commercial NLC mixtures and covering a variety of chemical compositions are given.

2. Materials

The alignment layers used in the experiments are fluorinated (ethylenic-cyclooxyaliphatic substituted ethylenic) copolymers (see figure 1). They are made by

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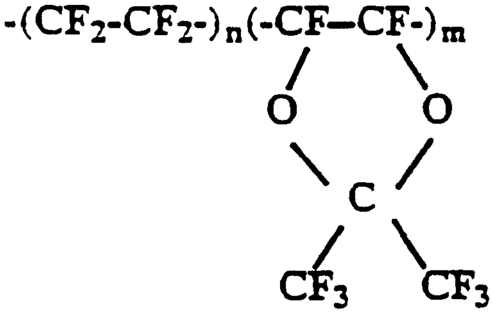

Figure 1. Chemical structures of perfluoropolymers on which thermally induced surface switching (TSS) was observed.

the copolymerization of tetrafluoroethylene (TFE) with bis-2,2-trifluoromethyl-4,5-difluoro-1,2-dioxole (TDD) [5]. Two copolymers are commercially available (Dupont De Nemours): the first contains approximately 65 wt% of TDD (P1) and the second 90 wt% of TDD (P2).

Both copolymers P1 and P2 are soluble in some common perfluorinated solvents, and mixtures of the copolymers in any proportion can easily be prepared.

3. Experimental

Copolymers P1, P2 or their mixtures are dissolved (0·5 to 1 wt%) in a mixture of the perfluorinated solvents Fluorinert (3M) FC-75, FC-40 and FC-43 in the ratio 90:5:5 by weight, respectively. These solutions are then deposited by spin coating on a clean glass or ITO covered glass substrate at a speed of 2000 to 3000 rpm. The solvents are removed by heating, in an air circulating oven, at 250°C over a period of 20 min. We obtain polymer layers 50 to 100 nm thick depending on the concentration and the spinning speed. The polymers are then gently rubbed using a velvet coated cylinder, in order to induce a tilted alignment in the initial homeotropic state and an homogeneous planar alignment in the planar state when heated. By choosing the rubbing directions, we can obtain different types of optical modes used in LCDs such as twisted nematic (TN), guest–host (GH) with parallel or antiparallel alignment, nematic–cholesteric phase change (ncPC) with various twist angles in the planar state. For GH cells, rubbing directions are antiparallel if not specified. Calibrated 9 μm diameter glass fibres were deposited on one of the substrates and then the cell was assembled under pressure and sealed with an UV polymerizable glue. The cells were filled by capillary action under vacuum. The NLCs used were commercial mixtures from Merck. For comparison, cells with standard homeotropic alignment were obtained by treating the surfaces with 3-(trimethoxysilyl)propyl-dimethyl-octadecylammonium chloride (Petrarch Systems) and with standard planar alignment using a rubbed polyimide, pyralin 2545 (Dupont) layer.

The measurements were made using a polarizing microscope fitted with a photomultiplier. For heating and cooling, either a Mettler hot stage FP-52 with the programmator FP-5 unit or a circulating thermostat with a home-made hot stage were used. The heating and cooling speeds were 3°C min^{-1}. The temperature was monitored by a thermocouple placed close to the measurement cell. The optical signal from the photomultiplier and the temperature, from a digital thermometer, were recorded on an X–Y recorder. For electro-optical measurements, AC voltages (rms) with a frequency of 100 Hz were applied to the cells.

4. Results

4.1. *Thermal surface switching without an electrical field*

The reversible thermal surface switching (TSS) from homeotropic to planar alignment with polymer P2 is illustrated in figure 2 (see curve C) using the dichroic mixture ZLI 4530 in the GH mode and compared to the temperature behaviour of the same NLC in homeotropic (A) and planar homogeneous aligned cells (B). The initial alignment in the cell, with alignment layer P2, is homeotropic. When it is heated the transmission decreases, in a narrow temperature range, to reach the transmission of the planar aligned cell. Beyond this temperature the transmission of the cell behaves with temperature like that of the standard planar cell (B). When this cell is cooled, the alignment changes from planar back to homeotropic. Very often a small hysteresis in the optical transmission versus temperature (not shown in figure 2) is observed.

On curve C, we can distinguish three domains of temperature behaviour for the cell with a P2 alignment layer:

(1) $T < T_H$ the alignment is homeotropic;

(2) $T_H < T < T_P$ rapid transition from homeotropic to planar alignment. We call 'transition temperature T_{HP}' the temperature at which the transmission reaches 50 per cent of its initial value in the homeotropic state;

(3) $T > T_P$ the alignment is planar.

The T_{HP} values depend on the NLC and copolymer used. The influence on T_{HP} values of the copolymers P1, P2 and a mixture in the 1 : 1 wt/wt ratio, used as alignment layers in a GH cell, is illustrated in figure 3. From this figure we see that T_{HP} is lower with the P2 (C22) layer than with P1 (C21), and is intermediate for their mixture (C20).

The measured T_{HP} values on polymer P2 were always lower than on polymer P1 and their mixture which shows an intermediate T_{HP}, and other NLC mixtures used showed a similar behaviour. The copolymer with a higher TDD content (P2) gives the

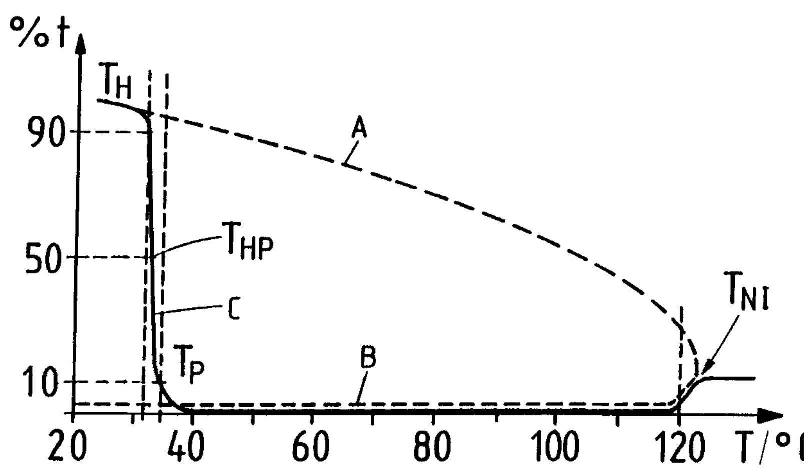

Figure 2. Transmission (per cent) as a function of temperature for three different cells filled with dichroic ZLI 4530 mixture (Merck). Polarizer parallel to the rubbing directions. Standard homeotropic alignment (A), standard planar alignment (B), reversible homeotropic–planar alignment (C).

lower transition temperature compared to the copolymer with a low TDD content (P1). The differences in the T_{HP} values obtained on P1 and on P2 are not the same for different NLC (see table 1).

The value of T_{HP} itself depends on the combination of NLC–copolymer as illustrated in figure 4 with polymer P1 and in figure 5 with polymer P2 as alignment layers. The same four NLC mixtures were measured in the GH (C1, C4) and TN (C5, C8) modes on P1 and P2 layers. The differences between the measured T_{HP} values on P1 and on P2 vary between 16°C (C4) and 44°C (C5) in this case.

The slope of the transmission curves as a function of temperature also depends on the NLC–copolymer combination. For the same NLC mixture, the copolymer P2 with the higher TDD content, gives a sharper transition curve than the copolymer P1.

The slope of the thermo-optical curve (transition curve) may be strongly influenced if we use an asymmetric cell: one alignment layer with P1 and the other with P2. In figure 6, transmission as a function of temperature is shown for such a cell and for symmetric cells with P1 and P2 layers on both sides of the cell. The transition curve of the asymmetric cell (P1/P2) is much flatter than those for the symmetric cells (P1/P1) and (P2/P2).

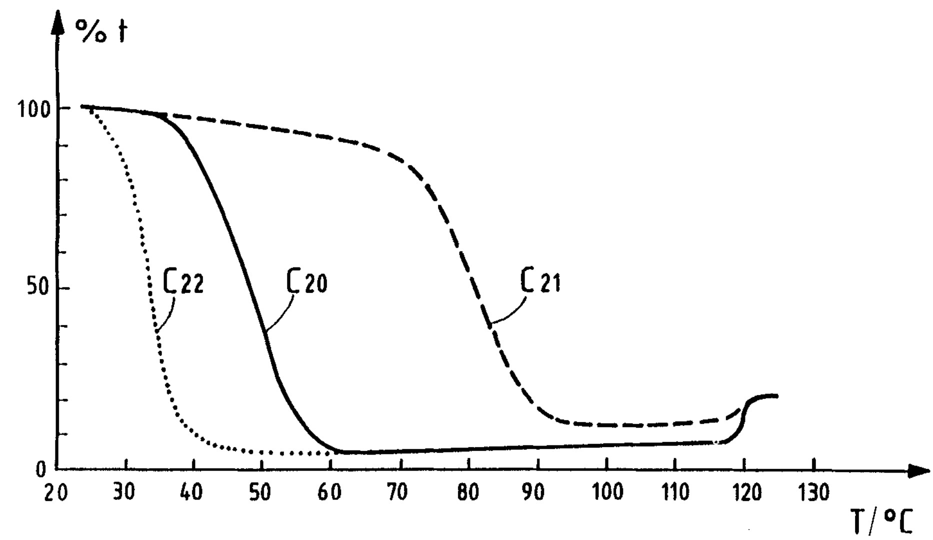

Figure 3. Transmission (per cent) as a function of temperature of the dichroic mixture ZLI 4530 in three different Heilmeier type cells with one polarizer parallel to the rubbing directions. The alignment layer is P1 (C21), a mixture (1:1 w/w) of P1 and P2 (C20) and P2 (C22).

Table 1. T_{NI}, T_{HP} and ΔT_{HP} values of some NLC mixtures measured in the TN mode with polymers P1 and P2 as alignment layers.

NLC	T_{NI}/°C	T_{HP}(P1)/°C	T_{HP}(P2)/°C	ΔT_{HP} (P1-P2)/°C
ZLI 3308	127	78	52	26
ZLI 3967	101	80	46	34
ZLI 4268	143	104	65	39
ZLI 3273	107	91	41	50
ZLI 3244	105	99	38	61

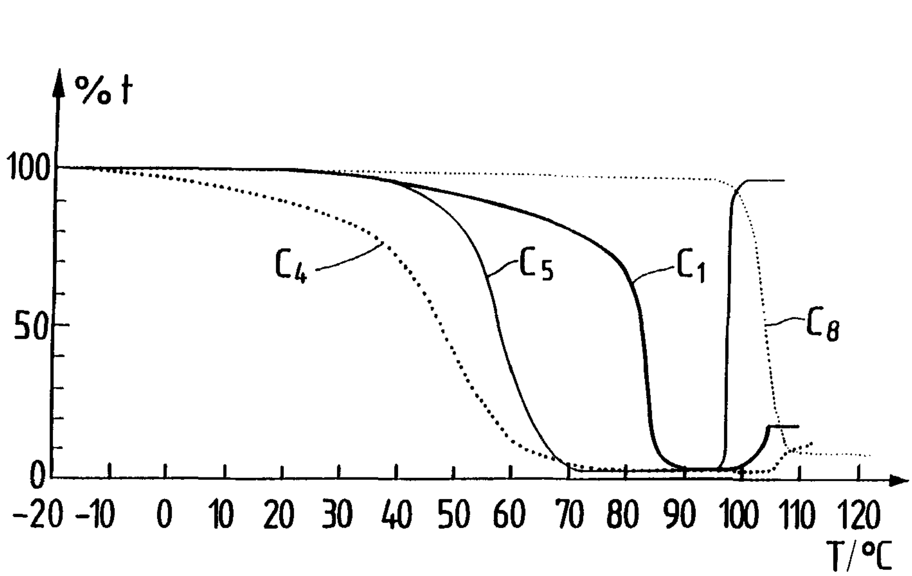

Figure 4. Transmission (per cent) as a function of temperature for different NLC mixtures in cells with alignment layer P1. Heilmeier type cells with one polarizer parallel to the rubbing direction filled with dichroic mixtures ZLI 4282 (C1) and ZLI 3284 (C4) and in TN type cells, with parallel polarizers filled with ZLI 4245-000 (C5) and ZLI 4268 (C8).

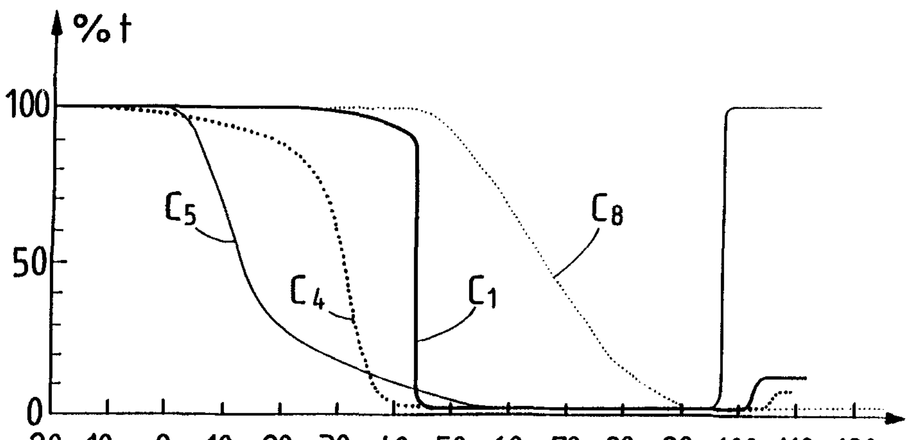

Figure 5. Transmission (per cent) as a function of temperature for different NLC mixtures in cells where the alignment layer is P2. Heilmeier type displays, with one polarizer parallel to the rubbing direction, filled with dichroic mixtures ZLI 4282 (C1) and ZLI 3284 (C4) and in TN type cells, with parallel polarizers, filled with ZLI 4245-000 (C5) and ZLI 4268(C8).

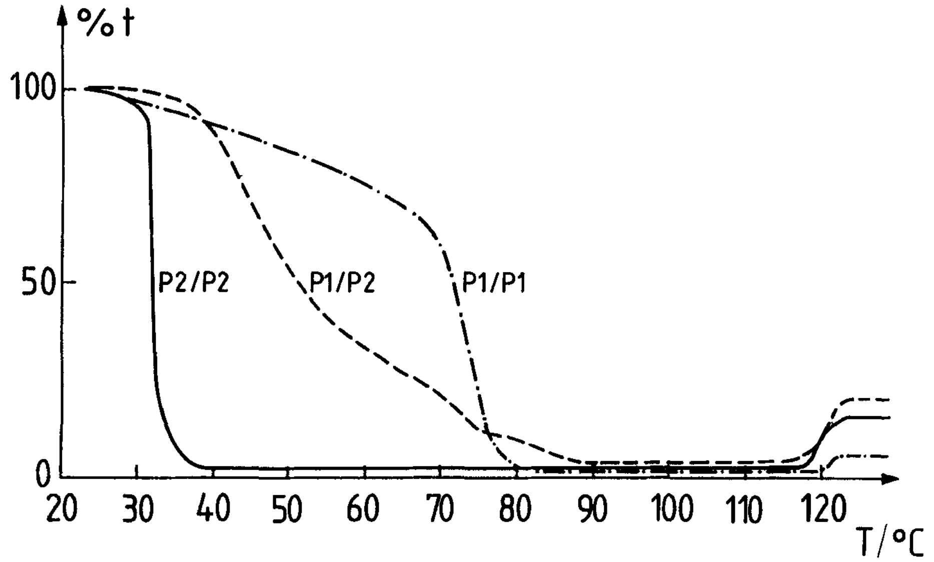

Figure 6. Transmission (per cent) as a function of temperature for three different Heilmeier type cells filled with dichroic mixture ZLI 4530 and with one polarizer parallel to the rubbing direction. Alignment layers are P1 on both sides (P1/P1) P2 on both sides (P2/P2) and P1 on one side and P2 on the other side (P1/P2).

This is due to the difference between the T_{HP} values of the two surfaces, one covered with P1 and the other with P2. The thermo-optical curve of this asymmetric cell looks like the electro-optical curve of a cell with homeotropic alignment on one side and planar alignment on the other side.

A correlation between the physical and chemical properties of the NLCs used and the experimental values of T_{HP} is not obvious. We observe that NLC mixtures with a high k_{33}/k_{11} ratio show low T_{HP} and often have a planar alignment at room temperature, while mixtures with a small k_{33}/k_{11} ratio are homeotropically aligned. In figure 7, the k_{33}/k_{11} from [6] ratio is plotted against the reduced transition temperature (T_{HP}/T_{NI}) obtained with the alignment layer P2. The corresponding NLCs with their physical properties, and their optically measured T_{HP} values are listed in table 2.

The trend of increasing T_{HP}/T_{NI} with decreasing k_{33}/k_{11} values is clearly seen in this figure, even though the k_{33}/k_{11} values used are given for 20°C, and different types of optical modes with different series of cells were used to establish this figure. In figure 7 there are some uncertainties due to experimental scattering from different series of measurement cells and to the variation of the k_{33}/k_{11} ratio with the temperature. A better correlation is expected with one series of measurement cells and the k_{33}/k_{11} ratio value determined at the transition temperature T_{HP}. The same trend is also shown with polymer P1 (not shown) with higher T_{HP}/T_{NI} values. Thus it is possible, by choosing the appropriate NLC–copolymer combination, to adjust the T_{HP} value for a given application.

TSS is a surface effect and accordingly boundary conditions have a strong influence on the optical characteristics of the transition from homeotropic to planar alignment. This is illustrated in figure 8, where the transmission curves of cells with the same P2 layers with one cell rubbed parallel (2) and the other antiparallel (1) are presented. In

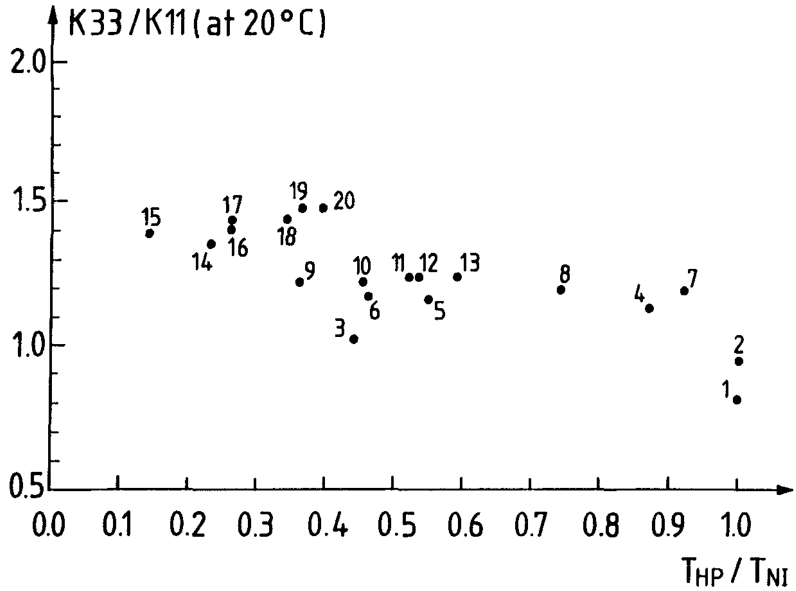

Figure 7. The ratio (K_{33}/K_{11}) of the bend to the splay elastic constants at 20°C as a function of reduced temperature T_{HP}/T_{NI}, the ratio of the homeotropic–planar transition temperature to the nematic–isotropic transition temperature, for different NLC (see table 2). The alignment layer is the polymer P2.

Table 2. T_{NI}, k_{33}/k_{11} and measured T_{HP} values of NLC mixtures aligned on polymer P2. The values of T_{NI} and k_{33}/k_{11} (at 20°C) are from [6] (see figure 7).

	ZLI No	T_{NI}/°C	k_{33}/k_{11} (at 20°C)	T_{HP}/°C	T_{HP}/T_{NI}
(1)	2583-000	66	0·81	~66	~1
(2)	3807	70	0·95	~77	~1
(3)	3561-100	73	1·02	32	0·44
(4)	2248	85	1·13	74	0·87
(5)	4245-100	95	1·16	52	0·55
(6)	3967	101	1·17	46	0·46
(7)	2975	76	1·19	70	0·92
(8)	2116-000	93	1·19	69	0·74
(9)	3244	105	1·22	38	0·36
(10)	4268	143	1·22	65	0·45
(11)	3101	86	1·24	45	0·52
(12)	3201-100	88	1·26	48	0·55
(13)	3449-100	91	1·26	54	0·59
(14)	3417-100	93	1·36	21	0·23
(15)	4245-000	96	1·39	13	0·14
(16)	3449-000	85	1·41	22	0·26
(17)	3417-000	94	1·44	24	0·26
(18)	3941	100	1·45	34	0·34
(19)	3284	92	1·48	33	0·36
(20)	3239	95	1·49	37	0·39

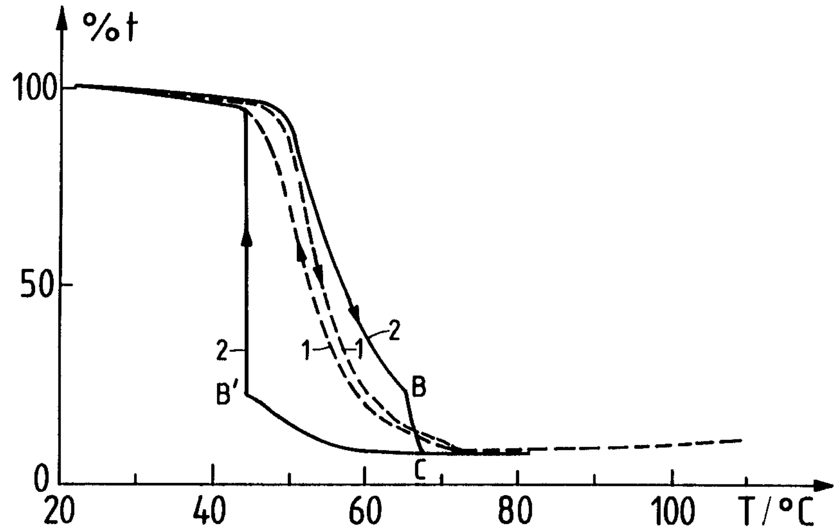

Figure 8. Transmission (%) as a function of temperature for two different Heilmeier type cells filled with the dichroic mixture ZLI 4530 and with one polarizer parallel to the rubbing direction. Curve 1 refers to the cell with antiparallel rubbing (tilt in the same direction) and curve 2 to the cell with parallel rubbing (tilt angles are opposite at the surface). For point B, B' and C, see figure 9.

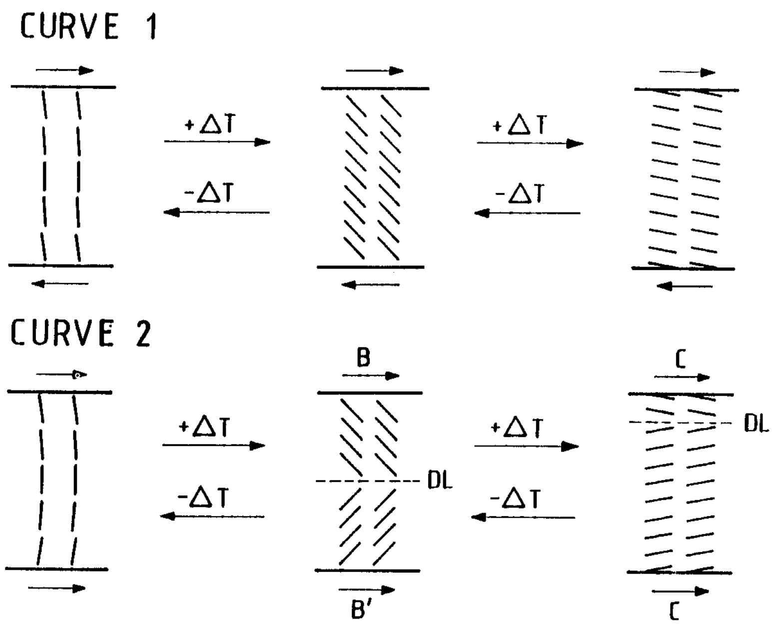

Figure 9. Schemes illustrating the orientation of molecules in cells 1 and 2 of figure 8. The arrows indicate rubbing directions, antiparallel in cell 1, parallel in cell 2. A dichroic mixture ZLI 4530 in the Heilmeier mode and the polymer P2 as the alignment layer were used. Configurations B, B' and C correspond to the points B, B' and C of figure 8. DL is the disclination line in the oppositely tilted cell 2.

cell (1), the alignment is tilted in one direction and in cell (2) in opposite directions (see figure 8). In cell (1), the transition takes place smoothly, both on heating and on cooling (see figure 9). The behaviour of cell (2) with reverse tilted boundaries is quite different, as illustrated in figure 9. During heating, up to the temperature B, the transition is continuous with a less steep curve than in cell 1. From point B to point C the curve is steeper. At point B, the cell has a configuration similar to that of the bistable cell described in [7], with a disclination line and a maximum of elastic energy. After the point B, the influence of one wall takes over (probably the hottest wall in contact with the heating plate) and the disclination line is pushed to the other wall. On cooling, the disclination line moves slowly, due to the higher energy requirements, where again the elastic energy is a maximum (B′). At this point, a very abrupt switching to the reverse tilted homeotropic alignment was observed. The tilt angles were estimated from the transmission measurements, at points B and B′ for different cells measured. They are the same for B and B′ points and around 54° from normal. So the points B and B′ correspond to the same state of orientation of the molecules. This reversely tilted cell (2) is an example of a thermally switching bistable cell.

4.2. *Thermal surface switching with an associated electrical field*

An electrical field can be associated with a TSS cell. In figure 10 the thermo-optical and electro-optical behaviour of a cell with a NLC of $\Delta\varepsilon > 0$ is shown in the TN mode. After thermally switching the cell from the homeotropic (clear) to planar (dark) state, the application of a small voltage reestablishes the clear state. A TSS cell with a NLC of $\Delta\varepsilon > 0$ can be switched electrically in the temperature range where the alignment is homeotropic ($T < T_H$). In figure 11, the thermo-optical curves of NLC mixture ZLI 4245-100 ($\Delta\varepsilon > 0$) are shown with two cells using P1 and P2 as alignment layers. Figure 12 illustrates the electro-optical behaviour of the same NLC for different temperatures on the P2 alignment layer. The Fréedericksz threshold becomes zero when the temperature is near T_H-homeotropic alignment domain.

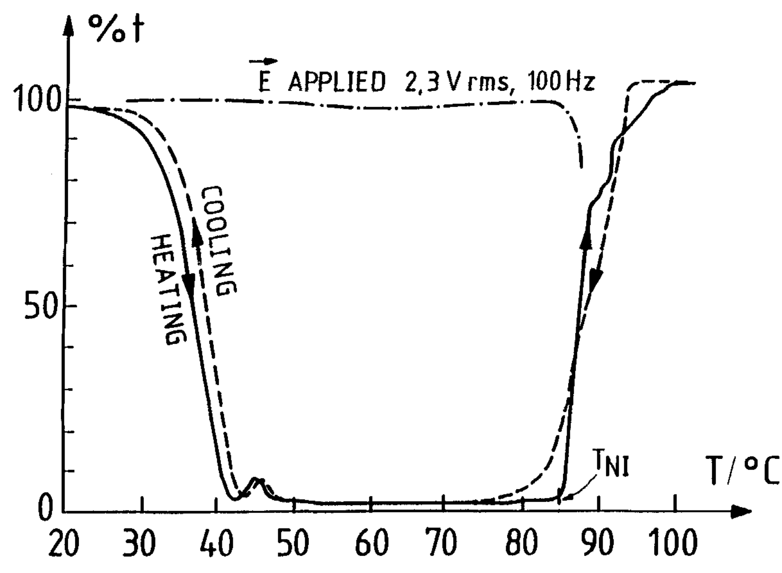

Figure 10. Transmission as a function of temperature in a TN type cell filled with ZLI 3449-000 ($\Delta\varepsilon > 0$) and parallel polarizers. Alignment layer is polymer P2.

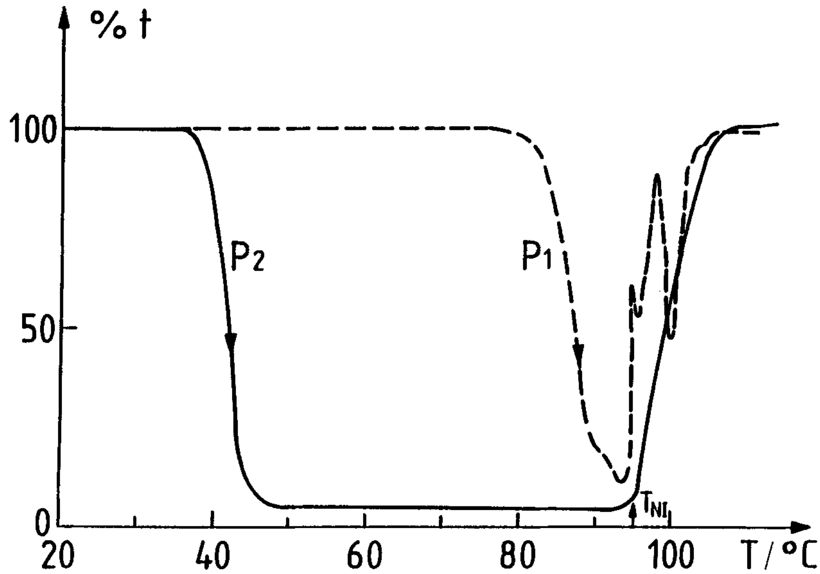

Figure 11. Transmission (per cent) as a function of temperature of two different TN cells with parallel polarizers and the NLC ZLI 4245-100 ($\Delta\varepsilon > 0$). Curve P1 holds for the cell with polymer P1 and curve P2 for the polymer P2 as the alignment layers.

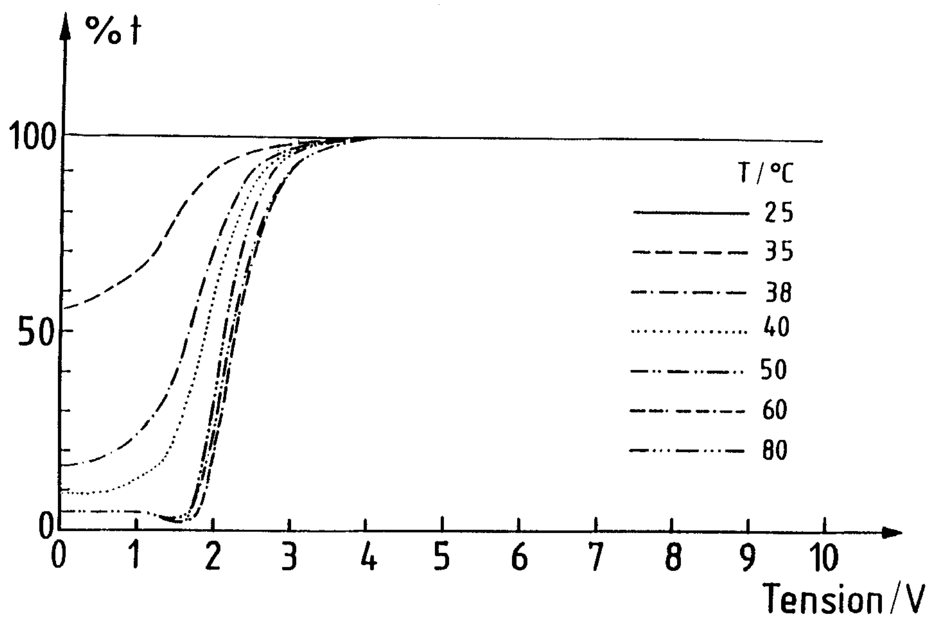

Figure 12. Transmission (per cent) as a function of applied voltage for different temperatures. The cell is TN type with parallel polarizers NLC ZLI 4245-100 ($\Delta\varepsilon > 0$) and polymer P2 as alignment layer are used. At room temperature the alignment is homeotropic.

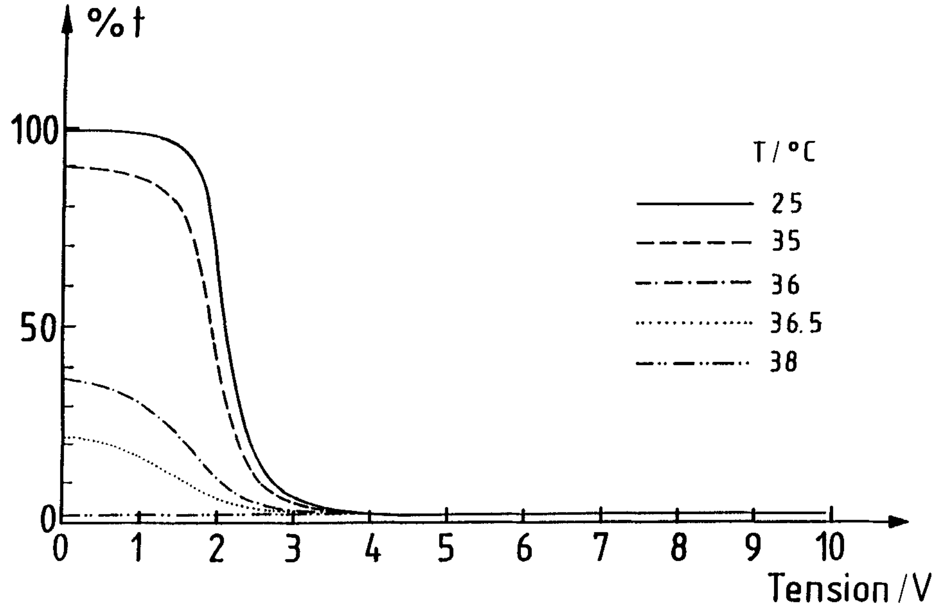

Figure 13. Transmission (per cent) as a function of applied voltage for different temperatures for a Heilmeier type cell with ZLI 4282 ($\Delta\varepsilon < 0$) on the alignment layer P2.The polarizer is parallel to the rubbing directions. Initial alignment, at room temperature, is homeotropic.

The electro-optical behaviour of a NLC with $\Delta\varepsilon < 0$, for different temperatures, is illustrated in figure 13. In the temperature range of homeotropic alignment ($T < T_H$), this cell gives electro-optical curves such as those for a conventional cell with homeotropic alignment. When the alignment becomes strongly tilted, around 35°C, the Fréedericksz threshold vanishes, and a continuous switching with increasing voltage appears. Beyond about 38°C, the orientation of the NLC is perpendicular to the electrical field and the alignment is planar.

5. Discussion

The TSS effect of NLCs was observed for a family of perfluorocopolymers containing a fluorinated chain with 5 membered side rings. These copolymers can be represented as intermediate compositions between two homopolymers, polytetrafluoroethylene (PTFE) and polybis-trifluoromethyldifluorodioxole (PTDD). The PTFE is an insoluble material, but can be deposited by plasma from TFE gas. The alignment of different NLCs on plasma deposited PTFE is homeotropic [8, 9]. The PTDD homopolymer is not commercially available so we have no experimental data on its aligning properties for NLCs. But we expect that it could be similar to that of the P2 copolymer with 90 wt% TDD content. In this family of copolymers we can imagine different compositions ranging from pure PTDD (TDD content 100 wt%) to pure PTFE (TDD content 0 wt%). Other compositions could also show the TSS effect.

From the experimental evidence, such as low T_{HP} values and steeper transition curves obtained with polymer P2 (TDD content 90 wt%) compared to polymer P1 (TDD content 65 wt%), the role of the TDD side ring seems very important for the

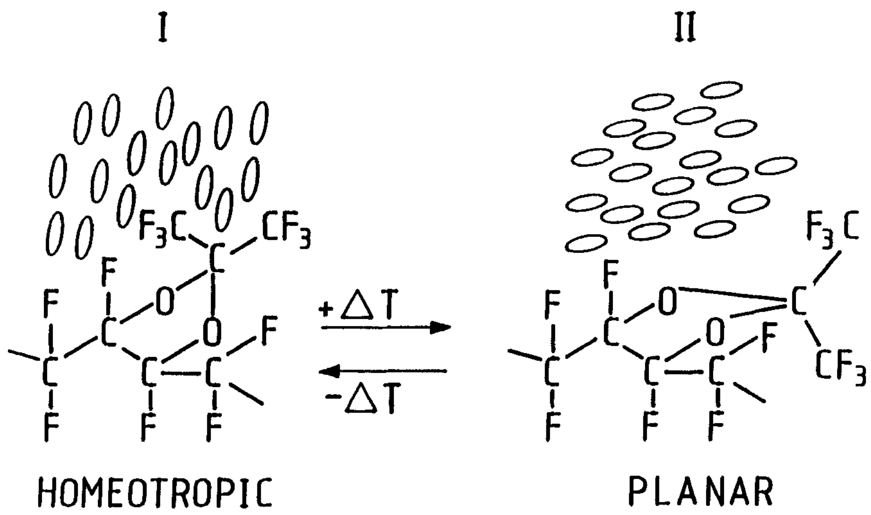

Figure 14. Possible structures of perfluoropolymers in the homeotropic and planar alignment. The change of conformation of the bent five membered ring by interaction with NLC, could change the polarity of the surface from less polar (I) to more polar (II) (see text for a tentative explanation).

occurrence of the TSS effect of NLCs. Supposing that the presence of the TDD ring is necessary for the observed TSS effect, we propose a hypothetical model which is sketched in figure 14.

According to this model, when the polymer layer P1 or P2 is deposited on a glass surface, the carbon atom bearing the $-CF_3$ group points out of the plane from other atoms of the ring forming a bent structure (I), like fluorinated surfactant molecules which orient their $-CF_3$ groups toward the air side. Such a boundary surface has a very low surface energy. A NLC mixture in contact with this low energy surface could initially align homeotropically [1]. When the temperature increases, the bent structure I changes by interactions with NLC molecules, to the other possible bent structure II exposing the four other more polar atoms of the ring system to the NLCs molecules. In the transition temperature range, around T_{HP}, the molecules tilt and become more or less oriented parallel to these four atoms. According to this hypothesis, the TSS effect could be due to the change from a non-polar to a more polar state of the surface as a result of the conformational change of the five membered ring of the TDD molecule in the presence of NLC molecules and under the influence of thermal energy. The two copolymers P1 and P2 used in this study have high glass transition temperatures (T_g), respectively T_g(P1) = 160°C and T_g(P2) = 240°C. Thus, at the temperatures at which we observe the TSS effect, the mobility of the polymeric backbone is low, especially with P2. Therefore, a conformational change of the polymer main chain is less likely to occur at these relatively low temperatures.

6. Conclusions

A thermally induced surface switching effect of nematic liquid crystals aligned on two copolymers of tetrafluoroethylene and bis-trifluoromethyldifluorodioxole, is observed. The swiching of nematic liquid crystals occurs from homeotropic alignment, at low temperatures to a planar alignment at higher temperatures. The inverse transition from a planar to a homeotropic alignment is obtained by cooling. The homeotropic to planar alignment transition occurs in a narrow temperature range and the transition temperatures depend on the nematic liquid crystal–copolymer combination used. NLCs with high k_{33}/k_{11} ratios require less thermal energy for the transition to occur and have lower reduced transition temperature (T_{HP}/T_{NI}) than with a low k_{33}/k_{11} ratio. The copolymer P2 with the higher bis-trifluoromethyldifluorodioxole content always gives lower transition temperatures than the polymer P1 with a low bis-trifluoromethyldifluorodioxole content. The slope of the transition curve is steeper with P2 than with P1 when used as alignment layers. The nematic liquid crystals aligned in these copolymers can be switched electrically either in their homeotropic or their planar temperature range as in a conventional cell.

The thermal surface switching effect is accounted for tentatively, by a modification of the surface polarity, from non-polar in the homeotropic state to more polar in the planar state. This modification could be due to a conformational change of the bis-trifluoromethyldifluorodioxole cycle between two bent structures under the influence of the nematic liquid crystal and thermal energy.

References

[1] Cognard, J., 1982, *Molec. Crystals. liq. Crystals* A, **5**, 1, supplement 1.
[2] Di Lisi, G. A., Rosenblatt, C., Griffin, A. C., and Hart, U., 1990, *Liq. Crystals*, **7**, 353.
[3] Flatischler, K., Komitov, L., Lagerwall, S. T., and Stebler, E., 1991, *Molec Crystals. liq. Crystals*, **198**, 119.
[4] Ichimura, K., Suzuki, Y., Seki, T., Hosoki, A., and Aoki, K., 1988, *Langmuir*, **4**, 1214.
[5] Korinek, P., 1991, *Matériaux et Techniques*, mars–avril, p. 41.
[6] Merck, E., 1989, *Commercial Liquid Crystal Mixtures* (Darmstadt).
[7] Thurston, R. N., 1985, *Molec Crystals. liq. Crystals*, **122**, 1.
[8] Sprokel, G. J., and Gibson, R. M., 1977, *J. electrochem. Soc.*, **124**, 557.
[9] Watanabe, R., Nakano, T., Satoh, T., Hatoh, H., and Okhi, Y., 1987, *Jap. J. appl. Phys*, **26**, 373.