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Back to the future: 30 years in challenging smectic liquid crystal displays and in clarifying scientific wonders

Atsuo Fukuda^a; Ichiro Kawamura^b; Y. Suzuki^c; T. Hagiwara^c; I. Kawamura^c; N. Okamura^d; T. Kitazume^d; M. Kakimoto^e; Y. Imai^e; Y. Ouchi^e; H. Takezoe^e; A. Fukuda^e

^a Department of Environmental Materials Science, Tokyo Denki University, Tokyo 101-8457, Japan ^b

Kawamura Laboratory of Organic Chemistry, 8-4-13 Tsukimino Yamato-shi, Kanagawa-ken, Japan ^c

Central Research and Development Laboratory, Showa Shell Sekiyu Co. Ltd., Kanagawa-ken 243-02,

Japan ^d Department of Bioengineering, Tokyo Institute of Technology, Tokyo 152, Japan ^e Department

of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo 152, Japan

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Back to the future: 30 years in challenging smectic liquid crystal displays and in clarifying scientific wonders

ATSUO FUKUDA*¹ and ICHIRO KAWAMURA²

¹Department of Environmental Materials Science, Tokyo Denki University, Tokyo 101-8457, Japan

²Kawamura Laboratory of Organic Chemistry, 8-4-13 Tsukimino Yamato-shi, Kanagawa-ken, 242-0002, Japan

A Commentary on the paper “New fluorine-containing ferroelectric liquid crystal compounds showing tristable switching”, by Y. Suzuki, T. Hagiwara, I. Kawamura, N. Okamura, T. Kitazume, M. Kakimoto, Y. Imai, Y. Ouchi, H. Takezoe and A. Fukuda. First published in *Liquid Crystals*, 6, 167-174 (1989).

1. How the research originated

It was 1975 when Meyer *et al.* [1] opened a new era by discovering that the chiral smectic C phase (SmC*) is a ferroelectric liquid crystal (FLC). In the same year, one of this Commentary's authors, Atsuo Fukuda, obtained a position in the Tokyo Institute of Technology and switched his research field from alkali halides to organic functional materials. Highly motivated by Meyer's insight into the bistability in helix-free FLC thin cells, Fukuda started to investigate the structure and properties of FLCs as one of the main themes of studying organic functional materials. Meyer wrote in his review article [2], “Especially interesting are the possible switching effects in very thin layers between conducting glass plates, in which surface pinning effects may be utilized to achieve an electro-optical memory.” It is clear from symmetry that there exist two energetically equivalent structures, with the smectic layers fixed perpendicular to the conducting surfaces, the helix unwound and the director uniformly aligned parallel to the surfaces. The optical bistability was also useful in realizing liquid crystal displays (LCDs) with large scale, high capacity, wide viewing angle and fast response, which were desired and believed to become key for flat panel displays. Hence in Japan not only Fukuda's group in the Tokyo Institute of Technology but also some groups in other academic institutions began to study the structure and properties of FLCs. Difficulties to overcome were how to synthesize FLC compounds and how to align them between two substrate glass plates. Collaboration between physicists and chemists was necessary in preparing FLC compounds; our paper selected for this 20th Anniversary Issue is a record

of a fruitful collaboration. The other author of this Commentary, Ichiro Kawamura, started to synthesize FLCs in Showa Shell Sekiyu K. K. and tried to increase their spontaneous polarization by adopting fluorine chemistry technology to replace $-\text{CH}_3$ with $-\text{CF}_3$ at the chiral carbon.

2. Challenging smectic liquid crystal displays

When the 8th International Liquid Crystal Conference was held in Kyoto in 1980, Clark and Lagerwall [3] reported that they had confirmed experimentally the bistable switching and proposed to use this for making attractive LCDs. Their presentation was so appealing that the shock extended beyond the academic community and many industrial people came to believe that the next generation of LCDs must be surface stabilized ferroelectric ones (SSFLCDs). Clark and Lagerwall coined the term “surface stabilization” to express properly the pinning effect referred to by Meyer. Segment-driven twisted nematic displays were already used in wristwatches and calculators, but a large majority in the LCD community felt it difficult to develop matrix-driven twisted nematic LCDs of good performance with respect to display size and information content. The enthusiasm to realize SSFLCDs was amplified by the prosperous state of the Japanese economy at that time. An unbelievably large number of chemistry-related companies entered into this project one after another, and tens of thousands of novel FLC compounds were synthesized. It would cost $\sim 10^4$ dollars at the very least to design and synthesize a new compound and to check its ferroelectricity in SmC*. The project was searching activities with $\sim 10^8$ dollars investment for FLC compounds and mixtures utilizable in SSFLCDs. Based on these abundant FLC

*Email: afukuda@seagreen.ocn.ne.jp

materials, various manufacturers in the electrical, optical and machinery industries prototyped SSFLCDs and noted that, “It is easier said than done”; the surface stabilized alignment of SmC^* could hardly be attained and the stable emergence of the ideal bistable switching was a rather fantastic idea [4].

Chemists naturally tried to increase the spontaneous polarization. Chisso Co. and Showa Shell Sekiyu K. K. synthesized homologous series of MHPOBC and TFMHPOBC, respectively, which have a spontaneous polarization as large as 1 mC/m^2 or more. Chisso Co. reported that, in the 1st International Conference on FLCs (Arcachon, 1987), the switching in MHPOBC exhibits a DC threshold probably due to the existence of an unknown phase [5]. About that time Kawamura proposed to Fukuda to make joint researches on the structure and properties of FLCs. The joint group soon published a paper describing a novel display principle based on tristable switching with a third stable state in addition to the well-known bistable states [6]. In 1989, Fukuda’s group clarified that the third state is the anticlinic, antiferroelectric, tilted smectic phase (SmC_A^*) and coined the term, antiferroelectric liquid crystal displays (AFLCDs) [7]. Kawamura sought much stronger and practical collaboration with Nippondenso Co., Ltd. to prototype the AFLCDs [8]; the fruit was exhibited as a prototyped 6-inch full-colour AFLCD at the 4th International Conference on FLCs (Tokyo, 1993) [9]. At the same place Citizen Watch Co. Ltd., also showed their prototyped black and white AFLCD [10]. Turning to the SSFLCD, Canon finally commercialized it as a 15-inch colour, “stylish FLC” in 1995 after a hard struggle to overcome the alignment difficulty, but stopped producing it just three years later in 1998. We can say retrospectively that, at around the year of FLC ’93 Tokyo, we were at the summit of R & D and full of confidence in commercializing attractive smectic LCDs. The tsunamis of thin film transistor (TFT) technology repeatedly struck the R & D front of smectic LCDs, swallowing the summit and crushed the confidence. Issues concerning viewing angle and response time appeared to give smectic LCDs an opportunity of going on stage [11], but in vain. Now the market is full of 32 inch or larger TFT-nematic-LCD television sets, although some SSFLCDs are used commercially in divers’ wristwatches with extremely low power consumption and in view-finders of a digital still camera with field sequential colour.

3. Clarifying scientific wonders

3.1. Anticlinic antiferroelectric SmC_A^*

The 30 years in challenging smectic liquid crystal displays cannot be considered fruitful from a technological

point of view. Scientifically, however, several unexpected structures and properties have been clarified in smectic liquid crystals and the 30 years are full of wonder. The discovery of the anticlinic smectic C_A^* phase (SmC_A) and its chiral antiferroelectric counterpart (SmC_A^*) was a surprising and fundamental finding in condensed matter [7, 12]. At that time it was taken for granted that the molecules tilt in the same direction and sense in subsequent layers [13] aside from a slight precession from layer to layer due to chirality, which results in the formation of a helical structure with the helix axis parallel to the smectic layer normal. In other words, it was hard to predict the existence of anticlinic SmC_A and SmC_A^* , where the molecules tilt in the opposite sense of the same direction from layer to layer with a possible helical structure due to chirality, as in SmC^* . An only exception was Beresnev *et al.* who tentatively proposed the anticlinic structure to explain their pyroelectric experimental results [14]. Chandani *et al.* confirmed the anticlinic SmC_A^* structure by noticing the difference in the helical structure between synclitic SmC^* and anticlinic SmC_A^* in the transmittance spectra of light incident obliquely to the helical axis [7]. The so-called full-pitch Bragg reflection band appears in SmC^* but not in SmC_A^* , although the ordinary selective reflection band emerges in both phases. This results from the fact that SmC_A^* does not lose the periodicity of half the pitch even in the oblique view while SmC^* surely loses it, indicating the appropriateness of the anticlinic structure on the visible light wavelength scale. On the molecular scale, the structure was directly confirmed by using resonant X-ray scattering [15] and other sophisticated techniques [16, 17]. Antiferroelectricity in SmC_A^* was proved by observing an electric current peak in an electric field-induced phase transition to ferroelectric SmC^* [7].

Another interesting aspect of the anticlinic SmC_A structure is that it allows the existence of very special topological defects, namely dispirations [18]. It is well-known that a SmC homeotropic cell shows the \mathbf{c} director schlieren texture. The strength of disclinations is normally restricted to $s = \pm 1$, because the tilt sense should be taken into account and $+\mathbf{c}$ is not equivalent to $-\mathbf{c}$. The \mathbf{c} director field is continuous everywhere except at the core line in $s = \pm 1$ disclinations, while it is discontinuous on the 2 dimensional surface in $s = \pm 1/2$ disclinations. The situation in SmC_A may differ from that in SmC because the \mathbf{c} directors in adjacent layers are oriented in the opposite sense, namely $+\mathbf{c}$ in one layer and $-\mathbf{c}$ in the neighbouring layers. Hence, the discontinuous two dimensional boundary, $+\mathbf{c} \neq -\mathbf{c}$, disappears if a screw dislocation with a Burgers vector of the same magnitude as the layer spacing exists at the

core of the defect [19]. This kind of complex defect consisting of a dislocation and a disclination is called a dispiration. The sponsor of this topological defect [18], Professor W. F. Harris in Rand Afrikaans University, was impressed with our paper reporting the first conspicuous example of dispirations and sent a letter addressed to Takanishi, Takezoe and Fukuda. He said, "It is great fun to see actual pictures of the dispiration that I described theoretically more than 20 years ago. I lost interest in the subject because then dispirations seemed to be structures of only academic interest. Now that you are finding examples it is tempting to take up the subject again."

The anticlinic structure, but not the antiferroelectricity, is the primary feature of SmC_A^* and its emergence is independent of chirality. Consequently, an important first step is to develop a molecular theory of achiral anticlinic SmC_A . A fundamental question is: What intermolecular interactions are responsible for the emergence of the anticlinic structure? The main difference in symmetry between SmC and SmC_A is the coupling between the translation and the director orientation. In SmC_A there is a glide plane which contains the layer normal and is perpendicular to the tilt plane. Hence we have to take into account the space symmetry group; it is important to consider the location of the symmetry axes. Two kinds of C_2 axes exist; one is in the middle of a layer perpendicular to the tilt plane, while the other at the layer boundary normal to the gliding plane. Since the tilt plane is a mirror plane in SmC_A as well as SmC , no spontaneous polarization emerges along the tilt plane normal. Whereas the C_2 axis at the layer boundary is not perpendicular to any mirror plane, there must be spontaneous polarization in the tilt plane along this axis. The coupling of this polarization with the tilt order parameter does stabilize SmC_A , but the effect is not strong enough to be responsible for the formation of the anticlinic structure [20, 21, 22].

It should be noted that antiferroelectric, anticlinic SmC_A^* was discovered during the experimental studies of chiral ferroelectric, synclitic SmC with large spontaneous polarization. The anticlinic structure must be determined by some molecular structural features that are typical of ferroelectric SmC^* with a large spontaneous polarization. One obvious structural element of this kind is the transverse dipole that is often located in the chiral alkyl chain close to the molecular end. Although the direct interaction between such dipoles vanishes after orientational averaging, the strong orientational correlations between such transverse molecular dipoles which are located in adjacent smectic layers may stabilize the anticlinic structure. These correlations are not sensitive to chirality, and are weakly affected by any

polar ordering. At the same time they can be sufficiently strong if the transverse dipoles are large and located close enough to each other in adjacent layers; their sufficient proximity appears to be assured by the experimentally observed fact that the chiral chain projects obliquely from the core. Osipov and Fukuda [22] presented a model interaction potential that stabilizes anticlinic SmC_A , proposed a particular molecular model based on the intermolecular orientational correlations between off-center transverse molecular dipoles, and obtained a simple phase diagram of the perfectly ordered smectic liquid crystal which contains SmA , SmC and SmC_A . The presented model is not in contradiction with existing experimental data, but we cannot exclude that in some cases SmC_A may be stabilized by some other specific interactions, in particular, steric ones [23].

3.2. Frustration between ferro- and antiferro-electricity

All of the interlayer interactions must be relatively weak, and this enables us to explain why SmC_A^* can be switched to SmC^* by applying a moderate electric field. The phase transition between SmC_A^* and SmC^* is first order and the system is frustrated between the synclitic ferroelectric and anticlinic antiferroelectric ordering. The frustration causes the temperature-induced sequence of phase transitions and produces various subphases. Many groups across the world have studied the subphases experimentally and presented their various views [24, 25]. Among them the following points are regarded as widely accepted: (1) There exists a uniaxial subphase, designated as SmC_z^* , which has a short pitch helical, and hence helielectric, structure [12, 26]; (2) Some materials show a first order phase transition between SmC^* and SmC_z^* , but in other cases the phase transition is not observed and a continuous evolution of the helical pitch takes place [27, 28]; (3) There exist at least two biaxial subphases with 3- and 4-layer periodicity [26]; (4) Both subphases are not planar, but their structures are quite biaxial and very different from the uniaxial clock model [15, 29, 30]; and (5) The 3-layer subphase is a rare but typical example of the ferroelectric phase observed not only in liquid crystals but also in condensed materials in general [29, 31].

Among several theoretical treatments, we believe, a model based on the novel discrete flexoelectric effect [32, 33, 34] together with the phase diagram that contains SmA , SmC and SmC_A [22, 24, 35] can answer the following three fundamental questions: (i) What are the long-range interactions which produce the non-planar structures? (ii) Why and how do the uniaxial and biaxial subphases emerge? and (iii) What is the role of chirality? Actually, however, the model has not yet been accepted as an established theory. Recent experimental

investigations using a photoelastic modulator clearly indicate that there exists at least one additional subphase other than 3- and 4-layer periodicity and that a phase transition is observed within the SmC_A^* temperature region [24, 25]. We would like to emphasize that these experimental facts support the aforementioned model. Consequently, it is particularly appropriate for Isozaki *et al.* to have specified the biaxial subphases by a fraction $q_T = [F]/([F]+[A])$, where $[F]$ and $[A]$ are the ferroelectric and antiferroelectric ordering within a period (unit cell) [25, 26, 35]. Since all of the biaxial subphases are closely related with SmC_A^* , Isozaki *et al.* designated them as $\text{SmC}_A^*(q_T)$ s; thus the traditional 3- and 4-layer subphases are called $\text{SmC}_A^*(1/3)$ and $\text{SmC}_A^*(1/2)$, respectively, and the fundamental phases, SmC_A^* and SmC^* , have $q_T=0$ and 1, respectively.

The frustration was also attractive from an application point of view [36, 37]. The electric field-induced continuous reorientation of a spatially uniform optic axis was observed as V-shaped switching or the thresholdless analogue optical effect in two kinds of mixtures consisting of some homologues of the prototype AFLCs, MHPOBC and TFMHPOBC, which were designated as the Inui mixture (later also called the Tokyo mixture) [38] and the Mitsui mixture [39]. The V-shaped switching was considered as the Langevin-type reorientation process of local in-layer directors, the tilt directions of which are randomly distributed from smectic layer to layer when no electric field is applied. The tilting correlation of the in-layer directors between adjacent layers was considered to be lost because of the extremely diminished energy barrier between SmC^* and SmC_A^* . When the sample has large spontaneous polarization or short helical pitch, a spatially uniform optic axis may also rotate continuously with an applied electric field [40, 41, 42]; it was not easy to confirm the Langevin-type reorientation process. At least in the Mitsui mixture, however, substrate interfaces destroy the anticlinic, antiferroelectric ordering and induce some randomization of in-layer directors; hence the observed V-shaped switching was concluded to be due to the Langevin-type reorientation process [43]. Because of its potential applications to TFT-LCDs, Mitsubishi Gas Chemical Co., Ltd. and Mitsui Chemicals, Inc. actively developed varieties of novel compounds and mixtures for V-shaped switching under the guiding principle of frustrating ferroelectricity and antiferroelectricity. Using these mixtures, Toshiba prototyped a 15 inch, full-colour, video rate LCD and exhibited it at the 1997 Toshiba Electronics Show [44]; Casio also showed a prototyped 5.5-inch, full-colour, video rate LCD at the Electronics Show '97 [45]. This time again, unfortunately, both companies were not successful in

commercializing these prototype LCDs. At the beginning of 2006, MGC finally stopped the R & D into smectics completely, and the last company that had retained an interest in the materials for TFT-smectic-LCDs has disappeared.

4. Epilogue

It has been reported that suitable materials for the V-shaped switching show an apparently single “ferrielectric” phase in the bulk over a wide temperature ($\sim 100^\circ\text{C}$) range [46, 47, 48]. The assignment is unacceptable, however, since the only ferrielectric phase whose existence is well established is the $\text{SmC}_A^*(1/3)$ subphase produced by the frustration and can emerge in a temperature range as narrow as $\sim 10^\circ\text{C}$ or less. In the binary mixture of such a “ferrielectric” compound with an antiferroelectric one, the boundary between them is peculiar in the sense that it is almost parallel to the temperature axis in the temperature-concentration phase diagram. When the subphases are typically observed, the boundary emerges quite differently. The characteristic boundary is interesting with respect to the complicated ordering of molecular dipoles in AFLCs, where two types of spontaneous polarization appear as described above, and is being studied by a group at Trinity College, University of Dublin. Aside from this, many scientifically fascinating subjects in smectic and related materials still lie at our feet. The structure and properties of smectic phases formed by the bent-core molecules, which Junji Watanabe at the Tokyo Institute of Technology proposed to Fukuda 15 years ago to study jointly, have now become one of the main topics in the 21st ILCC '06 Colorado. At the same time, it is true that the number of participants is drastically diminished in the session of the Japanese Liquid Crystal Society meetings dealing with the smectic-related subjects. Enthusiasm to realize smectic LCDs with passive or TFT electrodes has died down almost completely. When it comes to being close to an end, ...

“In me thou seest the glowing of such fire
That on the ashes of his youth doth lie
As the death-bed whereon it must expire,
Consumed with that which it was nourished by.
This thou perceiv'st, which makes thy love more
strong,
To love that well which thou must leave ere long.”
(From Shakespeare's sonnet LXXIII)

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New fluorine-containing ferroelectric liquid crystal compounds showing tristable switching

Y. SUZUKI†, T. HAGIWARA†, I. KAWAMURA†, N. OKAMURA‡, T. KITAZUME‡, M. KAKIMOTO§, Y. IMAI§, Y. OUCHI§, H. TAKEZOE§ and A. FUKUDA*§

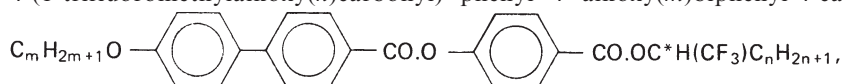
†Central Research and Development Laboratory, Showa Shell Sekiyu Co. Ltd., 123-1 Shimokawairi, Atsugi-shi, Kanagawa-ken 243-02, Japan

‡Department of Bioengineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

§Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

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To understand the real cause of stabilization of the third state and to assure the possible application of the tristable switching, we have studied the effect of chiral centers on the appearance of the third state, synthesizing (*R*)-(+)- and (*S*)-(–)-4-(1-trifluoromethylalkoxy(*n*)carbonyl) phenyl 4'-alkoxy(*m*)biphenyl-4-carboxylate



where $m=8, 9, 10,$ or 12 and $n=6$ or 8 ; note that the chiral centre has a trifluoromethyl group. By observing light transmittance and switching current responses to a triangular voltage wave and by taking stroboscopic micrographs, we have confirmed that all the materials synthesized show the tristable switching in wide temperature ranges; in particular, the materials with $m=10$ or 12 and $n=6$ have the stabilized third state even at temperatures below 30°C .

Significant advances in the surface stabilized ferroelectric liquid crystal displays (SSFLCDs) of Clark–Lagerwall type [1] have been presented at several conferences. However, it appears to be still annoyed with the selective pretilting of C-directors [2] due to the smectic layer bending (the chevron structure) and with the twisted states. The selective pretilting remarkably reduces the apparent tilt angle, i.e. the angle between the projections onto the substrate plate of the smectic layer normal and the director in the uniform states, and seriously deteriorates display contrast and/or brightness. In many FLCs manufactured for trial, moreover, bistable switching not between the uniform states but between the twisted states appears to have been used; hence the situation concerning display contrast and/or brightness may become even more unsatisfactory. The existence of the stable twisted states may also make worse the memory effect, particularly its threshold characteristics, in the switching between the uniform states.

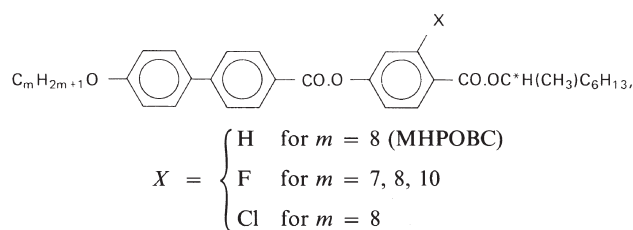
The SSFLCDs of Clark–Lagerwall type are really attractive, but the attraction is slightly diminished by

the requirement for cell thickness to be less than $2\mu\text{m}$ and by the chevron structure and the twisted states mentioned above [3]. On the other hand, the structure and properties of FLCs are so abundant in novelty that there exist great possibilities of using FLCs as functional materials, particularly for displays. Hence it is worth while searching for other switchings which can be used practically. In fact, several novel switchings have been proposed, such as tristable switching [4, 5, 6] switching via helicoidal structure [7], etc. [8, 9]. Among these the tristable switching [4, 5, 6] is particularly interesting because of the following characteristic features: (1) The so-called third state is spontaneously stabilized remarkably; a sharp DC threshold exists. (2) The extinction direction of this state is along the layer normal. (3) This state appears even in thick cells; the surface stabilization does not directly cause the third state. (4) The switchings from and to the third state occur at different voltages, showing hysteresis.

The third state was found in (*R*)-(+)- and (*S*)-(–)-4-(1-methylheptyloxycarbonyl) phenyl 4'-octyloxybiphenyl-4-carboxylate (MHPOBC). Hiji *et al.* [4] and Chandani *et al.* [5, 6] attributed the origin of the third state to

*Corresponding author. Email: afukuda@seagreen.ocn.ne.jp

the largeness of spontaneous polarization and the resulting electrostatic interaction of polarization charges $\rho = -\text{div } P_s$, [10, 11] but this explanation is not correct at least in this simplest statement because an almost racemic mixture of (R) -(+)- and (S) -(-)-MHPOBC also shows the third state at lower temperatures [12, 13], though the possibility that the highly hindered rotation around the molecular long axis plays an important role cannot be denied. Furukawa *et al.* [14] also noticed, though not clearly realized the stabilization of the third state, that switching between the uniform states exhibits a DC threshold. They considered the DC threshold to be a property of unknown phase, S_Y^* , which is not miscible to S_C^* , S_1^* and S_F^* . Furukawa *et al.* confirmed the S_Y^* phase in the homologous materials,



and observed the transition enthalpy, though very small. Goodby and Chin [15] reported that the optically active isomers appear to exhibit a different mesophase morphology from the racemate; at least one of the two extra ferroelectric liquid crystal phases, X_1 , that the chiral compounds apparently possess may be

similar to the S_Y^* phase. Anyway the real cause of the third state is not clear at present.

The purpose of this paper is to study the effect of chiral centers on the appearance of the third state. Since the number of compounds which show the third state is rather restricted at present, an increase in the number must be effective in clarifying the real cause of the third state and in assuring the possible application of tristable switching to a wide variety of optical devices. As a first step, we replaced the methyl group in the chiral centre of MHPOBC by the trifluoromethyl group and synthesized the homologous compounds shown in figure 1. Preliminary studies on branches of the trifluoromethyl type was made by Goodby and Leslie [16]. A few FLC compounds having the trifluoromethyl group in the chiral center were reported by Yoshino *et al.* [17, 18]. So long as the authors are aware of, however, no one reported the tristability in these compounds.

The synthetic route is given in figures 2 and 3. Optically active 1-(trifluoromethyl)-alkanols **5**, **7** were prepared by the Grignard reaction of ethyl trifluoroacetate **1** with appropriate alkylmagnesium bromides **2**, followed by the asymmetric hydrolysis of the corresponding ester derivatives **4** with enzymes of microbial or animal origin [19]. Ethyl trifluoroacetate **1** was added dropwise to a solution of the Grignard reagents at a temperature below -50°C . The hydrolysis was carried to less than 45 per cent with Lipase MY (*Candida cylindracea*) to obtain the alcohols with high optical purity greatly enriched in the (R) -enantiomers **5**. The (S) -enantiomers **7** were prepared from recovered

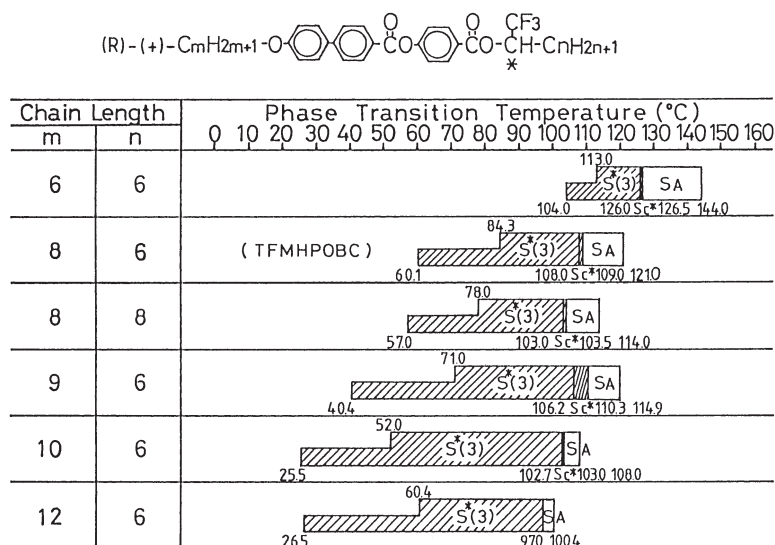


Figure 1. Phase sequences and transition temperatures of (R) -(+)-4-(1-(trifluoromethylalkoxy)(n)carbonyl) phenyl 4'-alkoxy(m)bi-phenyl-4-carboxylate.

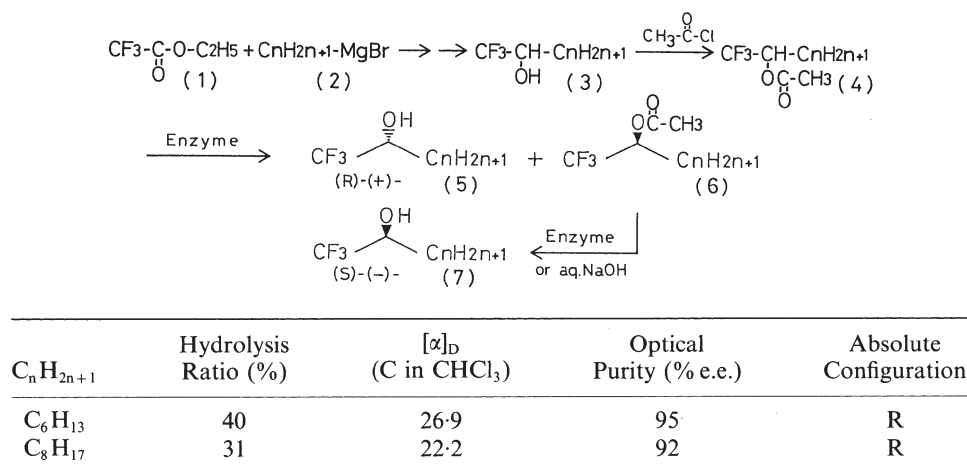


Figure 2. Synthetic route of optical active compounds.

acetates **6** by hydrolysis using a Cellulase (*Trichoderma viride*) and/or by the chemical method. The optical purity was determined by ^{19}F -N.M.R. signal intensities of the diastereomers which were derived from (*R*)- α -methoxy- α -(trifluoromethyl) phenylacetic acid chloride and optically active 1-(trifluoromethyl)-alkanols **5**, **7**.

Series of FLC compounds were synthesized by the esterification of 1-(trifluoromethyl)alkyl 4-hydroxybenzoates **11** and 4-alkoxybiphenyl-4'-carboxylic acids **12** using a dehydrating reagent such as dicyclohexylcarbodiimide. 1-(Trifluoromethyl)-alkyl 4-hydroxybenzoates **11** were obtained by the reaction of 4-benzyloxybenzoyl chloride **9** and (*R*)-(+)-1-(trifluoromethyl)alkanol **5** in pyridine at room temperature. 1-(Trifluoromethyl)alkyl 4-benzyloxybenzoates **10** were converted to 1-(trifluoromethyl)alkyl 4-hydroxybenzoates **11** by the reduction using Pd-carbon catalyst in methanol. The obtained ferroelectric liquid crystal compounds were purified by recrystallizing from absolute ethanol several times. The

structure was confirmed by means of I.R., ^1H -N.M.R. and ^{19}F -N.M.R. spectroscopy.

All the synthesized compounds have the phase sequence of $\text{Iso} \leftrightarrow S_A \leftrightarrow S_C^*$; the temperature range of the ordinary S_C phase is rather narrow and is followed by the range designated $S^*(3)$ where the third state appears. The $S^*(3)$ range is very wide particularly in the cooling process when the supercooling is observed; a compound with $m=10$ or 12 and $n=6$ shows the tristability even at temperatures below 30°C . These results are summarized in figure 1. The melting point was measured by a DSC (Seiko DSC-20) and the phase sequence was determined by a polarizing optical microscope with a hot stage (Metler FP-82).

Homogeneously aligned cells of $2.1\ \mu\text{m}$ thickness were prepared by rubbing thin polyimide films coated on the substrate plates. The spontaneous polarization was measured by the triangular wave voltage method [20]. The frequency was 10 Hz and the amplitude was

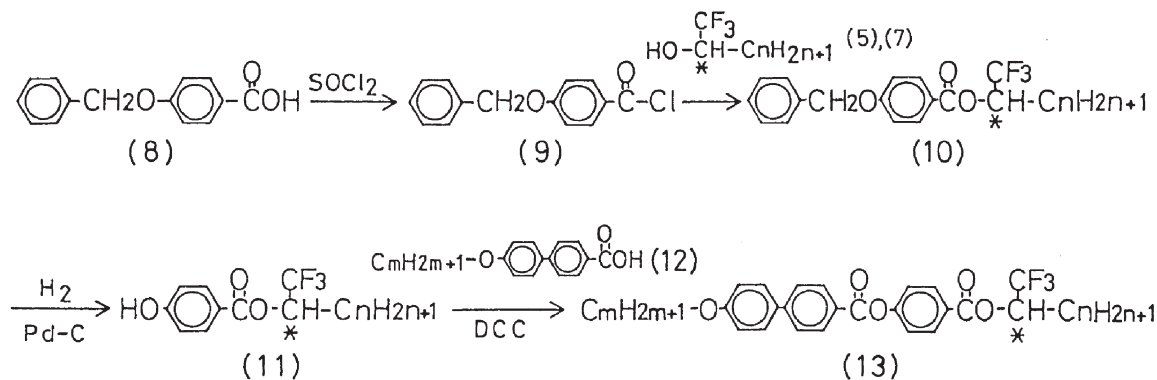


Figure 3. Synthetic route of FLC compounds.

± 30 V. Figure 4 shows an example of the current response in (*S*)-(+)-TFMHPOBC ($m=8$ and $n=6$), where the light transmittance response is also plotted; the crossed polarizers were set for one of the uniform states to be dark. The transmittance changes occur by two steps from one uniform state to the other. Switching current peaks appear at each instant of the transmittance changes. As was already pointed out by Chandani *et al.* [5, 6] and Furukawa *et al.* [13, 14] a DC threshold is clearly observed in the switching from the third state to the uniform state.

In spite of the DC threshold, the switching time from one uniform state to the other is rather fast when measured by reversing the applied voltage from +30 V to -30 V as illustrated for (*S*)-(+)-TFMHPOBC in figure 5. Figure 6 summarizes the temperature dependence of the spontaneous polarization of (*R*)-(+)-TFMHPOBC together with that of the corresponding non-fluorinated compound, (*R*)-(+)-MHPOBC. The spontaneous polarization increases monotonically as a function of $T_{AC}-T$ without showing any irregularities even at the temperature where the third state begins to appear [5, 6, 14]. The negative sign and the value observed in *R*-(+)-TFMHPOBC appear to indicate that the dipole moments on the carbonyl group and the chiral centre are not fully constructive in producing the spontaneous polarization. If both of the dipole moments were on the same plane, the resulted spontaneous polarization would be expected much larger.

To confirm the occurrence of tristable switching, stroboscopic micrographs were also taken using a similar apparatus described in a previous paper [21]. The cell of $2.4\ \mu\text{m}$ thickness was aligned by the method of 'epitaxial' growth from a spacer edge under a

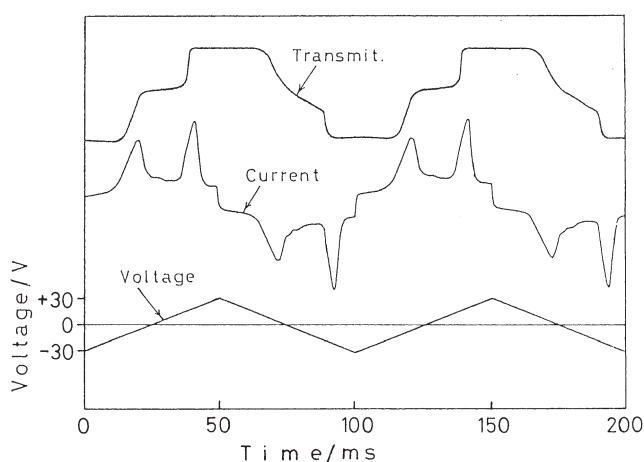


Figure 4. Light transmittance and switching current responses to a triangular voltage wave observed at 90°C in the $S^*(3)$ temperature range of (*R*)-(+)-TFMHPOBC ($m=8$ and $n=6$).

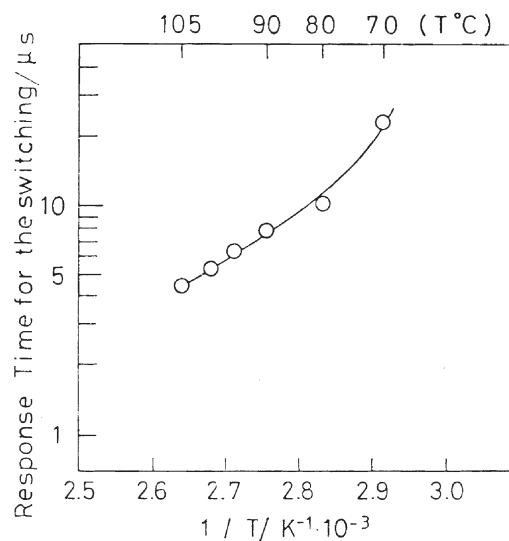


Figure 5. Temperature dependence of switching time between uniform states measured by reversing the applied voltage from +30 V to -30 V in (*R*)-(+)-TFMHPOBC.

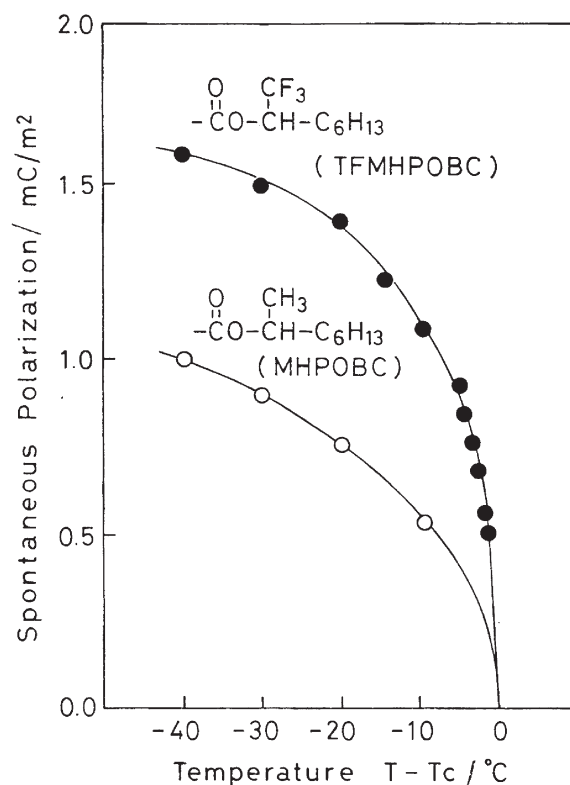


Figure 6. Temperature dependence of spontaneous polarization in (*R*)-(+)-TFMHPOBC and (*R*)-(+)-MHPOBC.

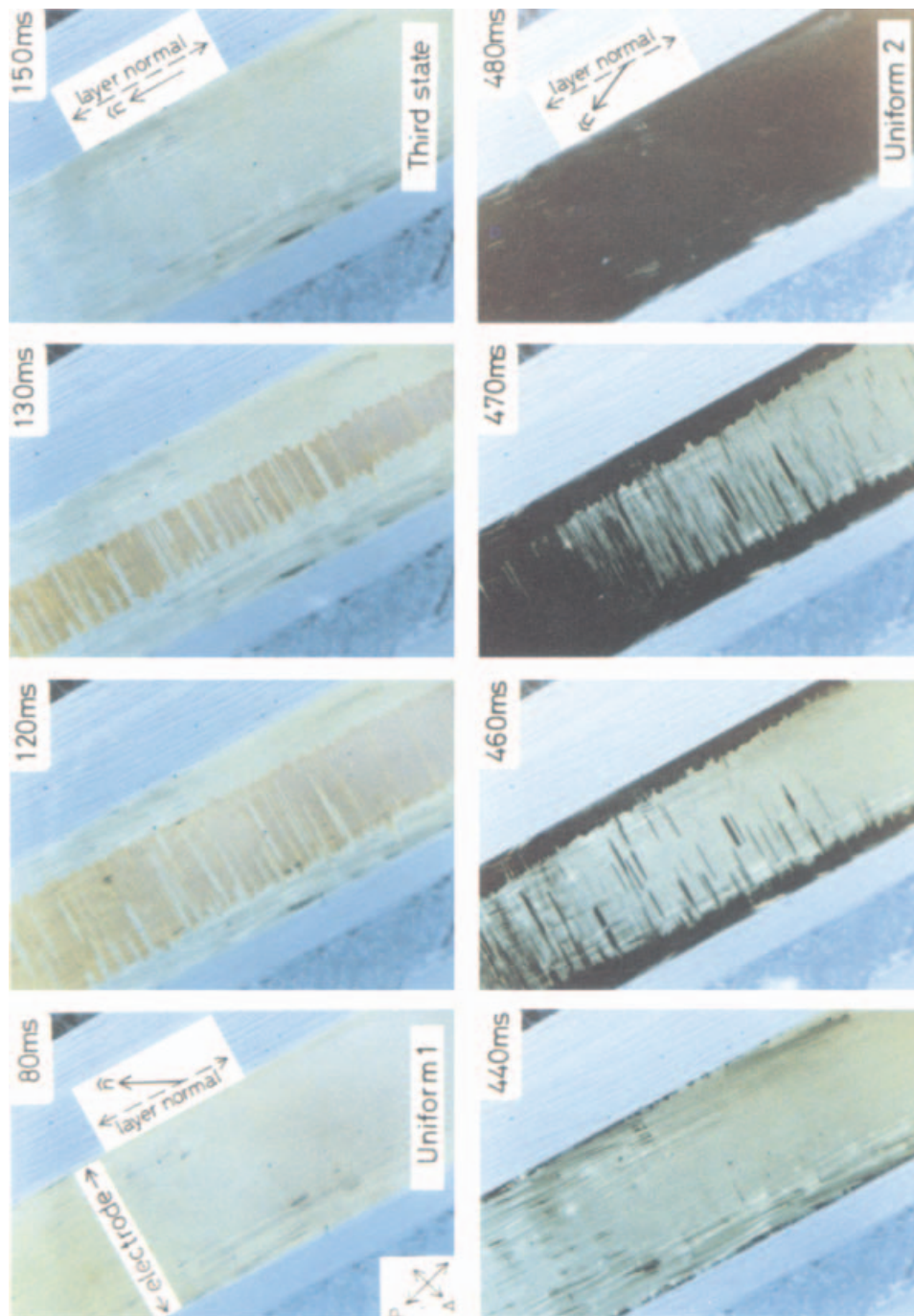


Figure 7. A series of micrographs taken stroboscopically during the switching from one of the uniform state to the other via the third state at 90°C in the $S^*(3)$ temperature range of $(R)\text{-}(+)\text{-TFMHPOBC}$. The applied voltage changes from -30 V at 0 ms to $+30\text{ V}$ at 500 ms , becoming 0 V at 250 ms .

temperature gradient which assures its high quality [22]. The electrodes should be shorted during the growth because the large spontaneous polarization may deteriorate the cell quality. A series of micrographs taken at 90°C by applying $\pm 30\text{ V}$ triangular wave voltage at 1 Hz is shown in figure 7. Zigzag

defects [3] were observed in the cell when it is virgin, after applying voltages, however, the cell is characterized by a series of lines almost parallel to the layer normal. When the crossed polarizers are set for one of the uniform states to be dark, the lines are not conspicuous in the uniform states but become

clearly observed during the switching between them; see the micrographs at +22.8 V (440 ms) and +25.2 V (460 ms).

The tristable switching occurs via the third state between the two uniform states. At -20.4 V (80 ms) the cell takes one of the uniform state. As the voltage decreases its negative value, the third state begins to appear as domains of characteristic shape mainly from both edges of the electrode; the domains are bars or elongated rectangles parallel to the smectic layer. The uniform state region is gradually squeezed into the middle part of the electrode area as illustrated in micrographs at -15.6 V (120 ms) and -14.4 V (130 ms) and finally disappears completely as shown in a micrograph at -12.0 V (150 ms). The whole electrode area is covered by the third state.

As already mentioned above, a DC threshold exists in the transition from the third state to either of the uniform state. In fact, the third state is quite stable and no change takes place until +22.8 V (440 ms), where the other uniform state begins to appear. The domain nucleation and growing processes as well as the resulted domain shape are quite similar to those described in the preceding paragraph as illustrated in micrographs at +25.2 V (460 ms) and +26.4 V (470 ms). The third state gradually squeezed into the middle part and finally disappears. The electrode area is covered with the uniform state at +27.6 V (480 ms). We are in the process of detailed studies, trying to understand the real cause of the third state[†].

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[†] Note added in proof.—Recently we confirmed that the third state is a novel antiferroelectric chiral smectic phase [23].