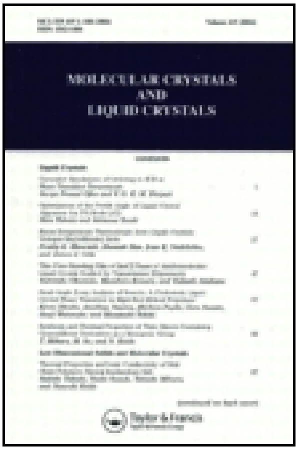

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New Ferroelectric Liquid Crystals with Spontaneous Polarization Exceeding 10^{-7}C/cm^2 and Their Electrical and Optical Properties

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New Ferroelectric Liquid Crystals with Spontaneous Polarization Exceeding 10^{-7}C/cm^2 and Their Electrical and Optical Properties

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New series of ferroelectric liquid crystals with neighbouring chiral carbons or a chiral carbon with C—Cl binding next to the molecular dipole moment (C═O) are synthesized utilizing isoleucine, valine, leucine, amylalchol and 2-amino butanoic acid as starting materials and are found to possess extremely large spontaneous polarization exceeding 3×10^{-7}C/cm^2 and dielectric constants larger than 7000. These compounds are found to exhibit a novel dielectric behaviour such as hysteresis in the temperature dependence due to the strong molecular interaction with surfaces. The response of electro-optic elements prepared with these ferroelectric liquid crystals is found to be very fast, in the μsec range, even at room temperature.

Keywords: ferroelectrics, liquid crystals, ferroelectric liquid crystals spontaneous polarization, electro-optic effect, dielectric constant

I. INTRODUCTION

The discovery of ferroelectricity in the chiral smectic C phase of DOBAMBC (p-decyloxybenzylidene-p′-amino-2-methylbutylcinnamate) by Meyer et al.,[1] has attracted much attention as the first nonsolid ferroelectric material and many theoretical and experimental studies have been carried out.[2,3,4] The proposals of various types of electro-optic devices with a high response speed[5,6,7] also have stimulated the synthesis of new ferroelectric liquid crystals with large spontaneous polarization.[8,9,10,11,12,13]

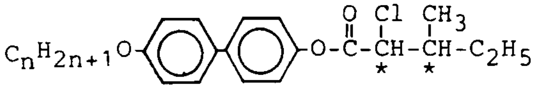
However, in most of these materials the spontaneous polarization is evaluated to be as low as the order of 10^{-9}C/cm^2, which is much smaller compared with the value expected from the completely aligned molecular dipole moment. This small spontaneous polarization is explained in terms of the rotation of the molecule around its long axis. Intramolecular rotation and vibration of the molecular dipole moment relative to the chiral part also reduces the spontaneous polarization, if the dipole moment (for example carbonyl group C=O in DOBAMBC) in a molecule is located far from the chiral part as in DOBAMBC. Relatively large spontaneous polarizations of the order of 10^{-8}C/cm^2 are observed in molecules with a dipole moment at the chiral part such as HOBACPC(p-hexyloxybenzylidene-p'-amino-2-chloropropylcinnamate) and DOBACPC (p-decyloxybenzylidene-p'-amino-2-chloropropylcinnamate).[10,11] We also have already reported that the spontaneous polarization exceeding 4×10^{-8}C/cm^2 can be obtained only by decreasing the separation between the chiral carbon and the molecular dipole moment.[12,13]

We have quite recently reported preliminarily the success of the synthesis of new compounds with spontaneous polarization exceeding 10^{-7}C/cm^2.[14,15] In this paper, we report the procedure of the synthesis and detailed electrical and optical properties of new series of ferroelectric liquid crystals with extremely large spontaneous polarization. The characteristics in electro-optic elements will be also discussed.

II. EXPERIMENTAL

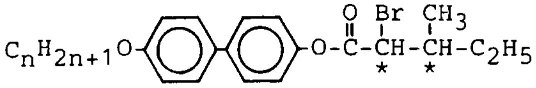
Figure 1 indicates molecular structures and their abbreviated names of the compounds used in this study. For the syntheses of compounds of series (A) and (B) in Figure 1, (2S,3S)-3-methyl-2-chloropentanoic acid, and (2S,3S)-3-methyl-2-bromopentanoic acid which were derived from isoleucine[16] were used, respectively. For the syntheses of compounds of series (C) and (D) in Figure 1, (S)-3-methyl-2-chlorobutanoic acid and (S)-3-methyl-2-bromobutanoic acid which were derived from valine,[16] were used respectively. Compounds of series (E) were obtained utilizing (S)-4-methyl-2-chloropentanoic acid which was derived from leucine.[16] (S)-2-methylbutanoic acid which was de-

(A)



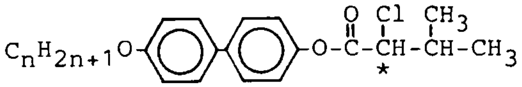
n=5:3M2CPPOB, n=6:3M2CPHOB, n=7:3M2CPHpOB,
n=8:3M2CPOOB, n=9:3M2CPNOB, n=10:3M2CPDOB,
n=12:3M2CPDDOB

(B)



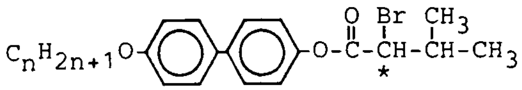
n=6:3M2BPHOB, n=8:3M2BPOOB, n=10:3M2BPDOB,
n=12:3M2BPDDOB

(C)



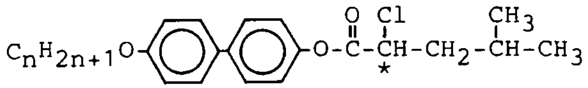
n=7:3M2CBHpOB, n=8:3M2CBOOB, n=10:3M2CBDOB

(D)



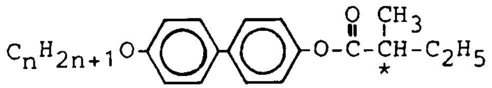
n=6:3M2BBHOB, n=8:3M2BBOOB, n=10:3M2BBDOB

(E)



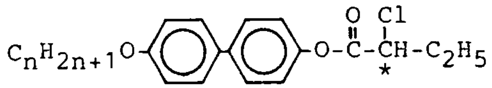
n=6:4M2CPHOB, n=7:4M2CPHpOB, n=8:4M2CPOOB

(F)



n=10:2MBDOB, n=11:2MBUDOB, n=12:2MBDDOB

(G)



n=6:2CBHOB, n=8:2CBOOB, n=10:2CBDOB

FIGURE 1 Molecular structures of new ferroelectric liquid crystals used in this study and their abbreviated names.

rived from amylalchol,[17] was used to obtain the compounds of series (F) in Figure 1. (S)-2-chlorobutanoic acid which was obtained from 2-amino butanoic acid was used to derive compounds of series (G) in Figure 1.

As a typical example of the synthetic procedure, the synthesis of 3M2CPOOB ((2S,3S)-3-methyl-2-chloropentanoic acid-4',4''-octyloxybiphenyl ester) will be explained; (2S,3S)-3-methyl-2-chloropentanoic acid (0.8 g), 4,4'-octyloxybiphenol (1.6g), N,N'-dicyclo-hexylcarbodiimide (1.1g) and 4-pyrrolidinopyridine (0.1g) were mixed in dichloromethane (50 ml) and left for about 12 hours at room temperature. After the precipitate was removed, the solution was evaporated to obtain a crude product. The product was purified by passing it through a chromatographic column of silica gel and by the recrystallization from hexane solution. NMR, IR spectra and elemental analysis were used to determine the molecular structures of final products.

The samples were sandwiched between two conducting (In-Sn oxide coated) glass plates, whose surface was rubbed in a direction for obtaining the homogeneous alignment. The spontaneous polarization was evaluated utilizing modified Sawyer-Tower method and also by the application of triangle-shaped voltage.

The dielectric constant was measured either by a capacitance bridge (TR-10C, Ando Denki) or by observing the current component whose phase was shifted by 90° from applied field with a lock-in-amplifier (PAR 5204). The results of both methods shows a good coincidence. The cell was mounted on an optical microscope stage for optical observations simultaneously with electric measurements.

The electro-optic effects in the cells filled with these new ferroelectric liquid crystals are studied by observing the change of the transmission intensity of He-Ne laser (6328 Å) through the cell with the application of voltage pulses.

III. RESULTS AND DISCUSSION

By the microscopic observations, the chiral smectic C (Sm C*) phase was clearly recognized in these materials. In the lower temperature range than the Sm C* phase, other chiral smectic phases were observed in some of them by the microscopic observation. Though some of these phases looks like Sm I* phase, they have not been classified definitely at this stage. In such cases, we marked them as the Sm* phase in this paper.

Figure 2 shows the temperature dependences of the spontaneous polarization of 3M2CPHpOB, 3M2CPOOB, 3M2CPNOB, 3M2CBOOB and 3M2CPDOB as examples. As evident from this Figure, these materials are found to possess extremely large spontaneous polarizations exceeding 2×10^{-7}C/cm^2 in the Sm C* phase, which is the highest value in ferroelectric liquid crystals so far reported. As also indicated in Figure 3 for example, the spontaneous polarization at lower temperatures even becomes larger than 3×10^{-7}C/cm^2. Other new materials obtained in this study also indicated large spontaneous polarizations.

The spontaneous polarization of ferroelectric liquid crystals so far reported has been estimated to be smaller by more than two orders of magnitude compared with the expected values from the molecular dipole moment, which has been interpreted in terms of (1) free rotation of liquid crystal molecule around its long axis and (2) intramolecular rotation or vibration of the molecular dipole moment relative to the chiral carbon. Relative large spontaneous polarization was observed in HOBACPC and DOBACPC[10,11] in which a dipole moment (C—Cl) was formed directly at the chiral carbon atom. In

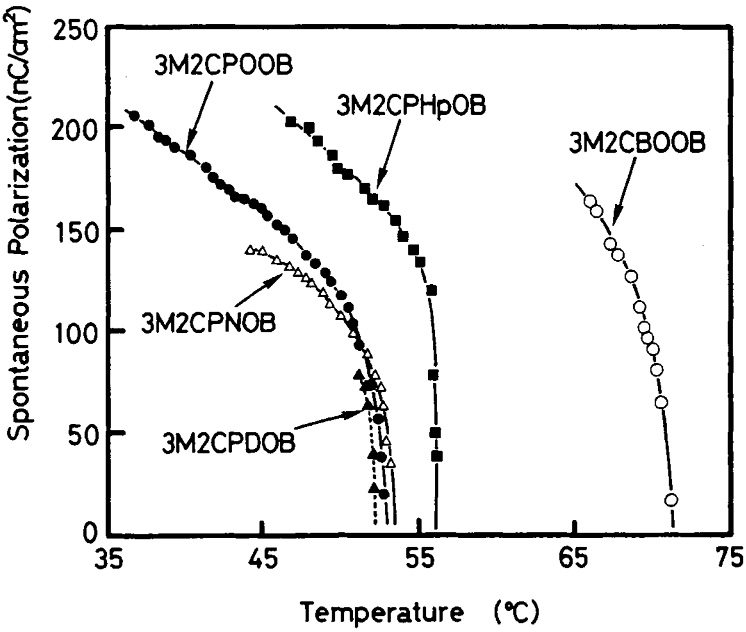


FIGURE 2 Temperature dependences of spontaneous polarizations of some examples of new ferroelectric liquid crystals in the chiral smectic-C phase.

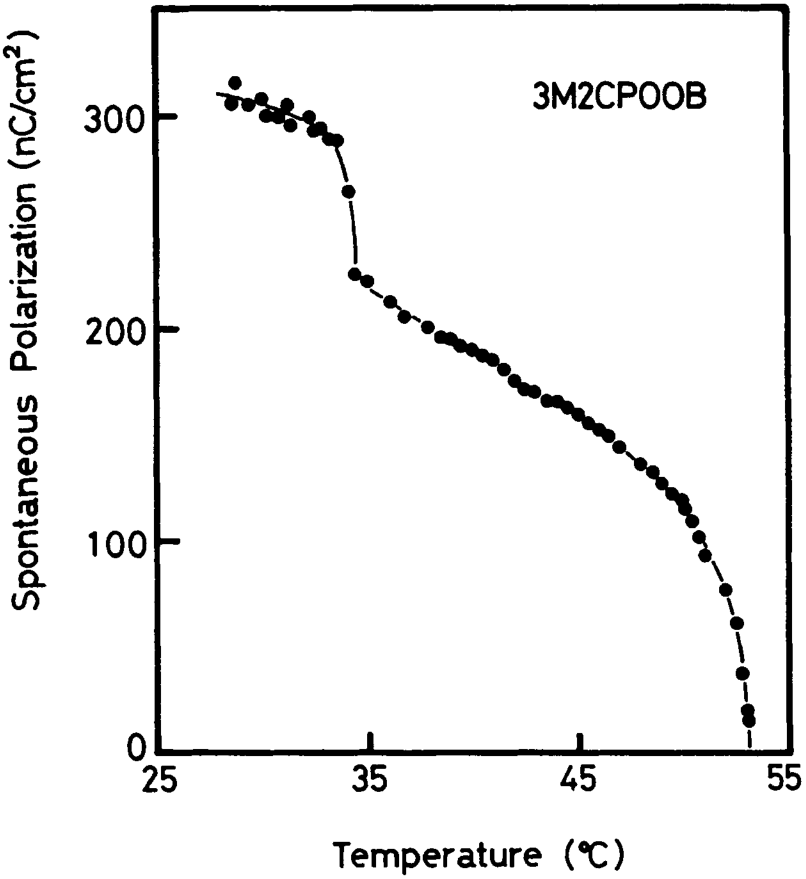


FIGURE 3 Temperature dependence of the spontaneous polarization of 3M2CPOOB in wide temperature range.

these cases, however, the contributions from dipole moments of C—Cl and C=O cancel due to the interaction between these two dipoles. Large spontaneous polarization was also obtained in DOBA-1-MBC (p-decyloxybenzylidene-p′-amino-1-methyl-butylcinnamate) and DOBA-1-MPC (p-decyloxybenzylidene-p′-amino-1-methylpropylcinnamate) by decreasing the separation between the chiral carbon and the dipole moment compared with DOBAMBC.[12,13]

In our new compounds a halogen atom is attached directly to the chiral carbon atom which is located next to the polar group (C=O) and in some cases two neighbouring chiral carbons are included in a molecule. The individual molecular dipole moment estimated from the spontaneous polarization observed in this study was about 0.5 Debye, which may indicate that the free rotation and the relative intramolecular motion mentioned above should be suppressed considerably, resulting in the enhancement of the spontaneous polarization.

The temperature dependences of the spontaneous polarization P_s can be described by the equation of $P_s \propto (T_c - T)^\beta$, where T_c is the transition temperature between the Sm A and Sm C* phases. The critical exponent β of these compounds was evaluated to be about 0.38 as shown in Figure 4, which nearly coincides with the value so far reported in other ferroelectric liquid crystals.

Figures 5, 6, 7, 8 and 9 show the temperature dependences of dielectric constant of 3M2CPHpOB, 3M2CPOOB, 3M2CPNOB, 3M2CPDOB and 3M2CBOOB. All of these data were measured during the cooling stage from the isotropic phase. Though the temperature dependence differs remarkably in the materials, it should be noted that the extremely large dielectric constants were observed in all these new compounds compared with that of DOBAMBC,[18]

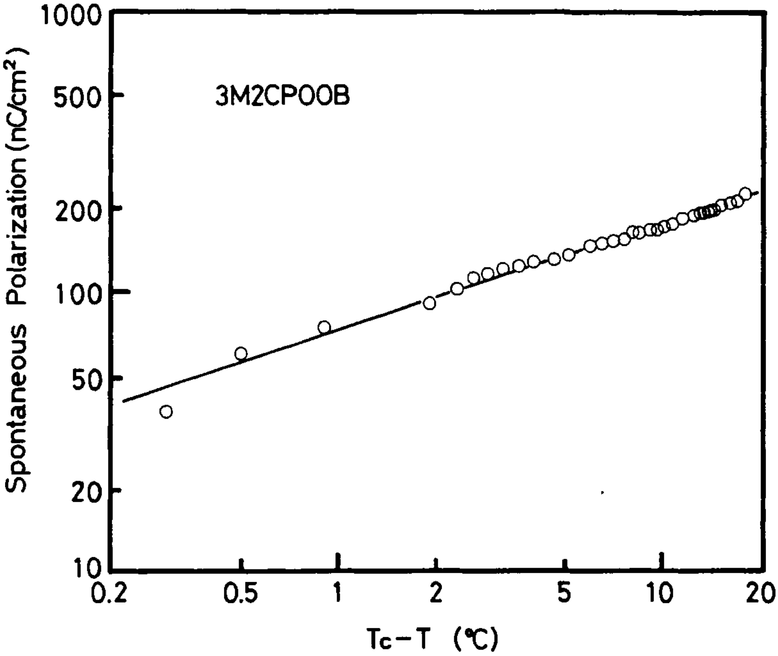


FIGURE 4 Logarithmic plot of the temperature dependence of the spontaneous polarization near the phase transition temperature T_c.

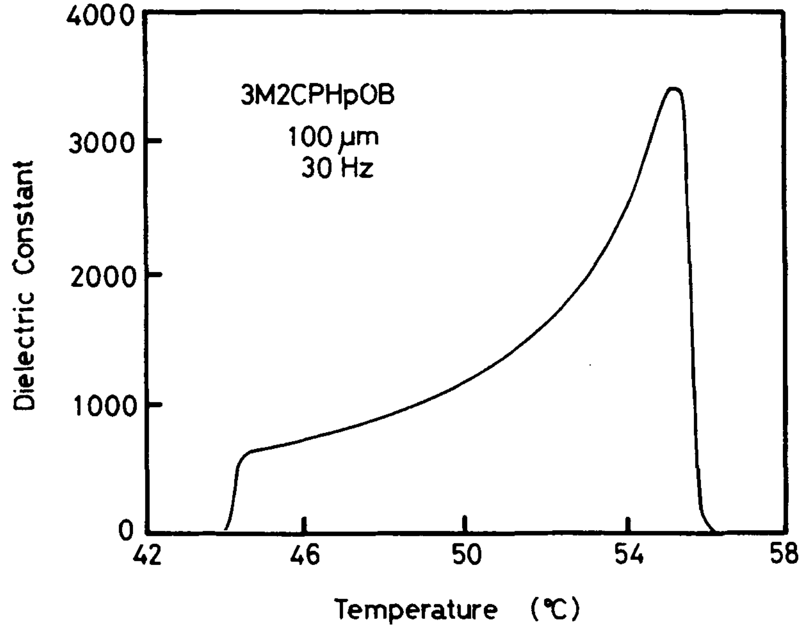


FIGURE 5 Temperature dependence of dielectric constant in 3M2CPHpOB.

which should be related to the large spontaneous polarization mentioned above.

The dielectric constant in the Sm A phase is small. However, with decreasing temperature it increases slightly and at the transition temperature T_c from the Sm A to Sm C* phase it increases steeply. The temperature dependence of the dielectric constant of 3M2CPHpOB is similar to that in DOBAMBC as evident from Figure 5.[18,19] Therefore, in the Sm A phase, close to T_c, the contribution of the soft mode (tilt angle vibration) seems to enhance the dielectric constant and in the Sm C* phase the contribution of the Goldstone mode (winding and unwinding motions of helicoidal structure) as well as the soft mode contribution should enhance the dielectric constant remarkably.

As evident from Figures 6 and 7, 3M2CPOOB and 3M2CPNOB exhibit novel dielectric behaviour which is different from that of DOBAMBC. In particular, the chiral smectic phase of 3M2CPOOB seems to be divided into three regions (A), (B) and (C) as shown in Figure 6. An optical microscope observation suggests that the region (C) is a higher ordered chiral smectic phase than the Sm C* phase and at the phase transition temperature T_{c2} between the region (B)

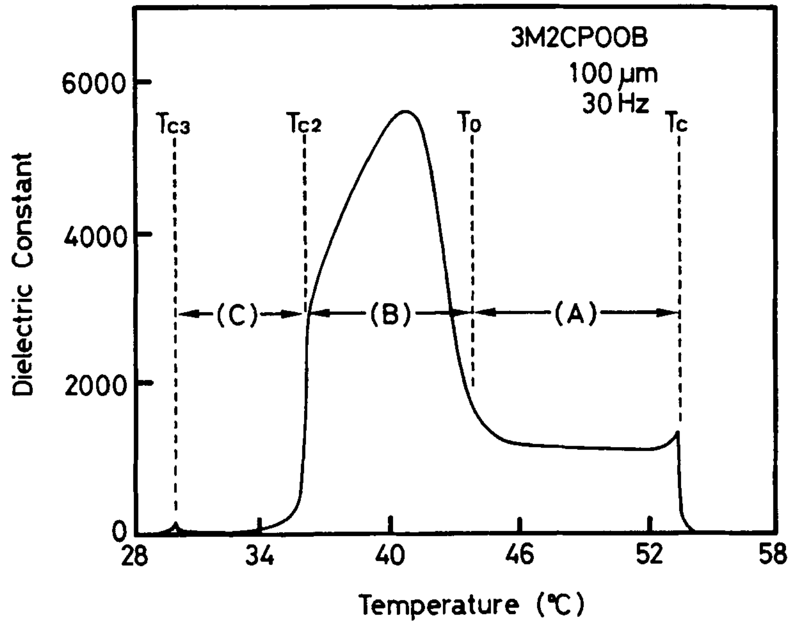


FIGURE 6 Temperature dependence of dielectric constant in 3M2CPOOB.

and (C), a small anomaly of dielectric constant was observed. The phase transition at T_{c2} is also evident in the temperature dependence of the spontaneous polarization shown in Figure 3. Since the region (C) is the higher ordered phase with higher viscosity compared with the Sm C* phase, the dielectric constant in the region (C) is evaluated to be smaller than that in the region (A) and (B) in spite of large spontaneous polarization as indicated in Figure 3. Similar smaller dielectric constant in the low temperature higher ordered phase was observed in DOBAMBC and HOBACPC.[11,18]

On the other hand, the thermal analysis suggested that the anomaly between the region (A) and (B) is not due to a phase transition.

As evident from Figure 10 there exists a remarkable hysteresis in the temperature dependence of the dielectric constant in 3M2CPOOB. When the sample was cooled down from the Sm A phase, the dielectric constant in the region (A) was much less than that in the region (B). However, when the sample was heated up again from the region (B) or (C), the dielectric constant increased monotonously and there did not exist any difference between dielectric constants in the region (A) and (B). Moreover, the clear disclination lines can be observed in the state of high dielectric constant i.e. in the region (B)

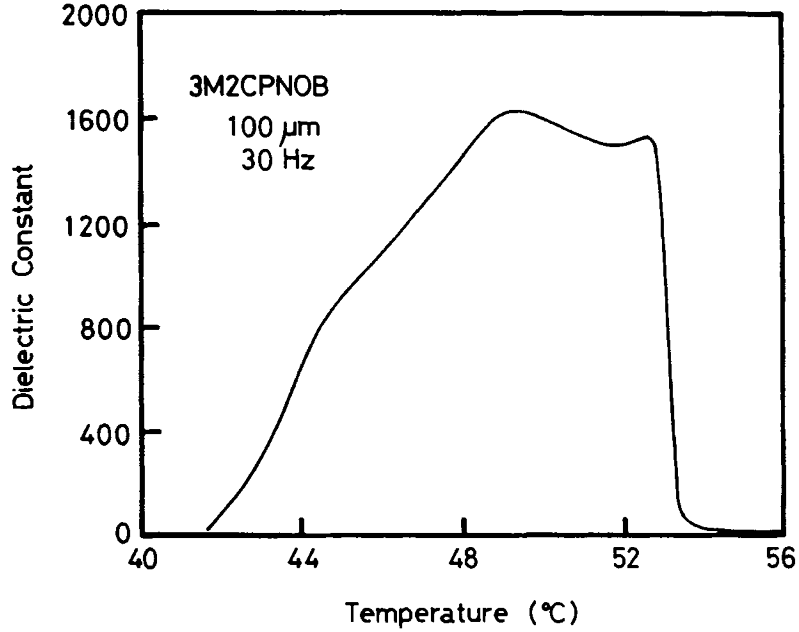


FIGURE 7 Temperature dependence of dielectric constant in 3M2CPNOB.

of the cooling stage and in the whole range of the heating stage. On the other hand, the clear disclination line was not observed in the state of low dielectric constant, i.e. in the region (A) of the cooling stage.

The temperature dependence of the dielectric constant was also found to depend strongly on the cell thickness as shown in Figure 11. As evident from this figure, the critical temperature T_0 decreases with decreasing cell thickness, suggesting that T_0 is not a real phase transition temperature. These experimental results may be interpreted as follows.

When the sample was cooled down into the region (A), a strong molecule-surface interaction prevents the formation of the helicoidal structure in whole of the sample, especially near the surface region. Therefore the small contribution of the Goldstone mode results in the smaller dielectric constant. In the lower temperature range (B), the intrinsic winding force originated from chirality will be stronger than the unwinding force due to the surface effect, resulting in the establishment of helicoidal structure. In this case, the contribution of the Goldstone mode should become predominant, giving the enhancement of the dielectric constant. If once the helicoidal structure

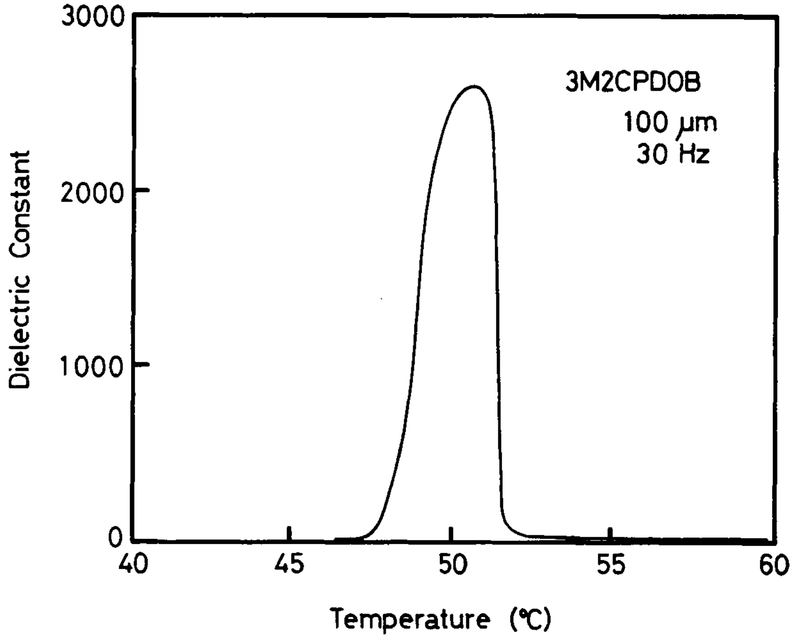


FIGURE 8 Temperature dependence of dielectric constant in 3M2CPDOB.

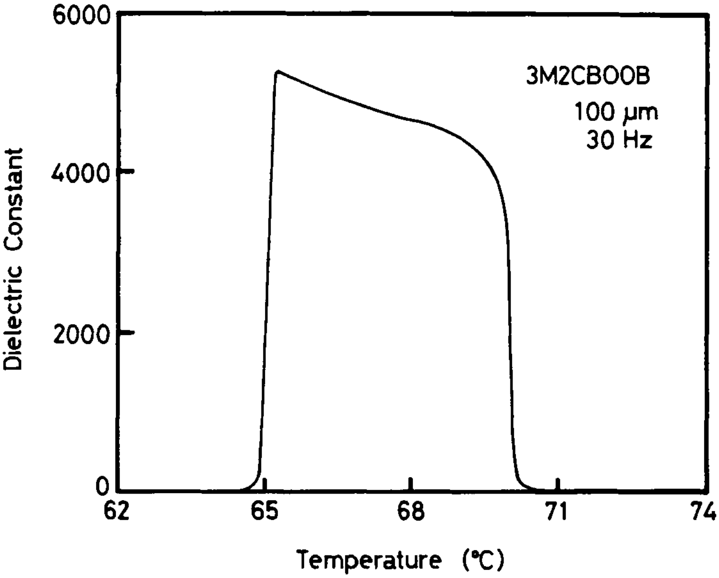


FIGURE 9 Temperature dependence of dielectric constant in 3M2CBOOB.

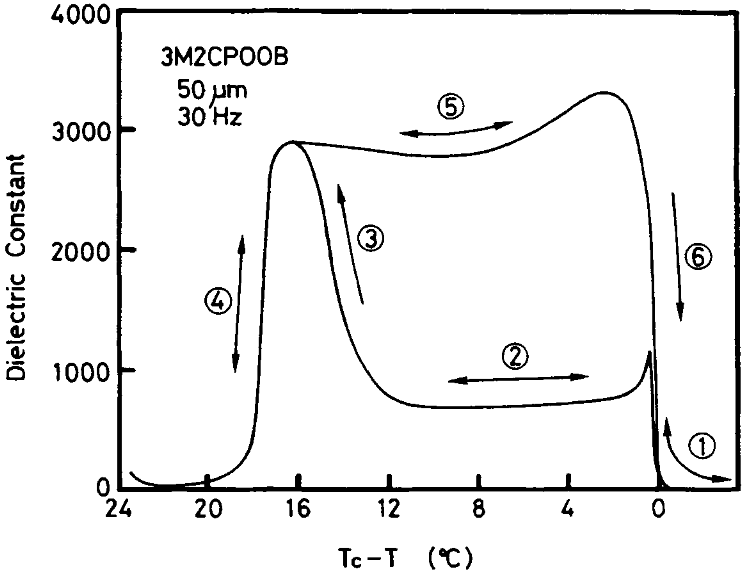


FIGURE 10 Hysteresis of temperature dependence of dielectric constant in 3M2CPOOB.
Cooling stage: 1 → 2 → 3 → 4
heating stage: 4 → 5 → 6

was established in whole of the sample, it was not unwound even by heating up into the region (A) again and the large dielectric constant was maintained until the transition temperature T_c as shown in Figure 10. However, it is not clear at this stage why in 3M2CPOOB such strong surface effect was observed even in relatively thick cell (for example 100 μm), contrary to other conventional ferroelectric liquid crystals in which the surface effect appears in much thinner cells.

By mixing these ferroelectric liquid crystals with various materials we could prepare ferroelectric liquid crystal mixtures with the wide temperature range, the phase transition temperature to solid state lower than −20°C and the spontaneous polarization of the order of 10^{-7}C/cm^2. Details of these mixtures will be reported in near future.

These new ferroelectric liquid crystals also showed novel electro-optic effects.

As already reported, there are several types of electro-optic effects in ferroelectric liquid crystals.

1. Electro-optic effects utilizing difference of light transmission between wound and unwound states of helicoidal structure.[5]

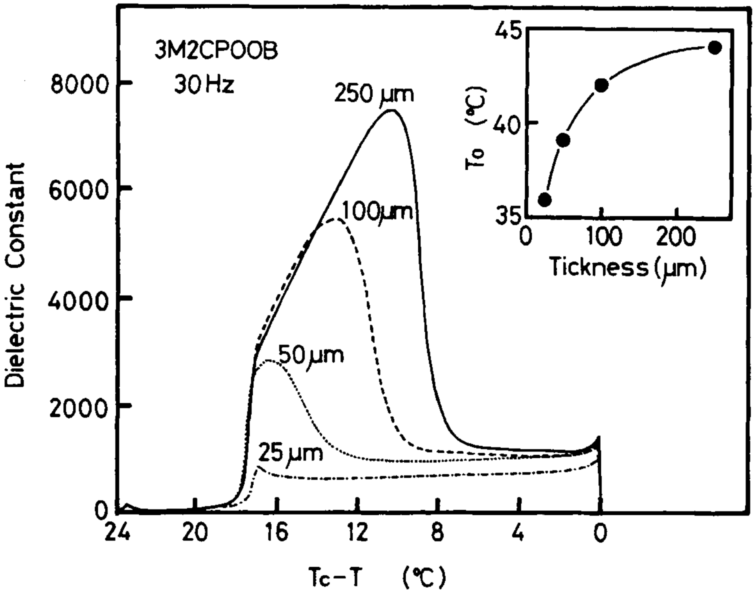


FIGURE 11 Temperature dependence of dielectric constant in 3M2CPOOB as a function of sample thickness.

Inset: Dependence of the critical temperature T_0 on cell thickness.

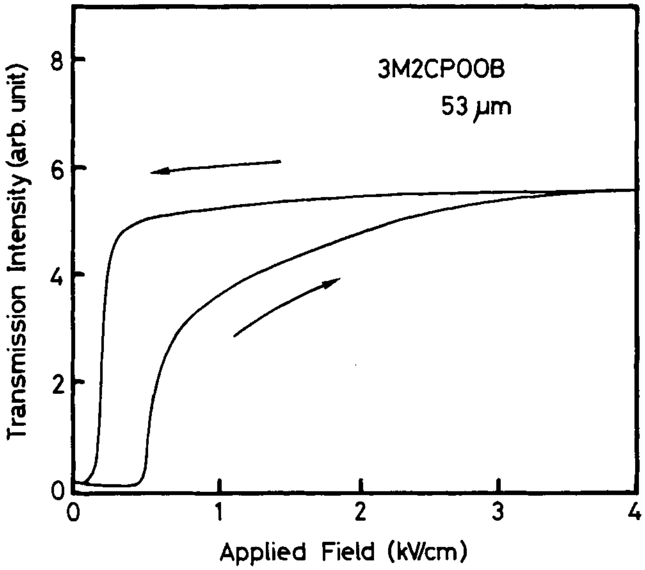


FIGURE 12 Dependence of the transmission intensity through a thick cell (53 µm) of 3M2CPOOB on the applied field.

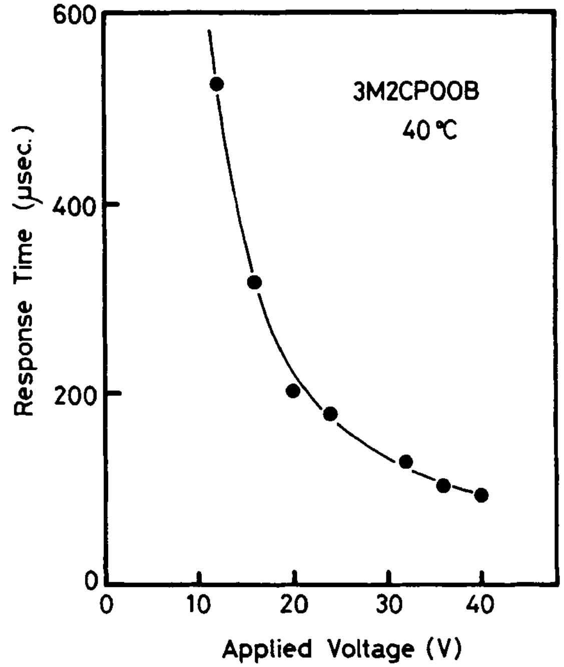


FIGURE 13 Dependence of the response time of the transmisson change through the electro-optic cell of type 1 (unwinding of helicoidal structure) in 3M2CPOOB on applied voltage.

2. Electro-optic effects utilizing birefringence change of ferroelectric liquid crystal in the thin cell.[6,7]
3. Electro-optic effects utilizing the transient light scattering at the instant of domain switching, which have been named TSM devices.[20,21]

The type (1) effect is the most simple and does not need any optical polarizer. However, in conventional ferroelectric liquid crystals, the threshold field was relatively high and the response time was relatively long (several tens msec). However, in these new series of compounds, the threshold voltage was found to be very low, even less than 1KV/cm as shown in Figure 12 and the response time was found also to be very short as shown in Figure 13. These facts indicate that even most simple type (1) electro-optic cell can be used practically because of the reasonable low threshold voltage and high response speed.

In type (2) and (3) electro-optic effects, the response time less than several tens of μsec was also observed. For example, Figure 14 indicates the voltage dependence of the rise time of TSM cell (type (3)

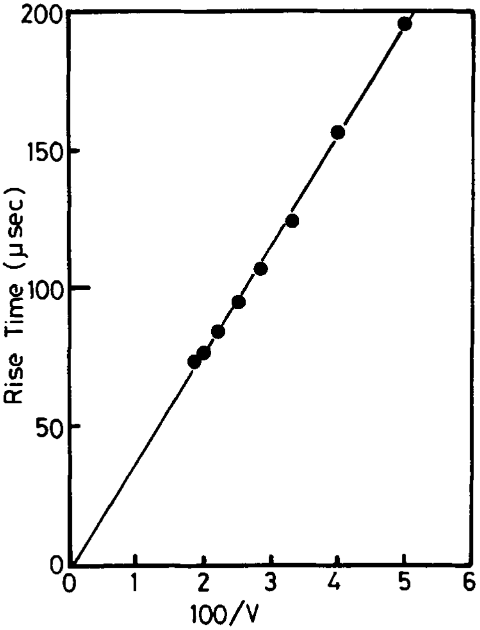


FIGURE 14 Dependence of the rise time of transmission change of the electro-optic cell of type 3 (TSM) by with the mixed ferroelectric liquid crystals on applied voltage (25°C).

effect) utilizing a mixture of these ferroelectric liquid crystals at room temperature. Figure 15 also shows the rise time of the optical switching element of type (2) (SSFLC cell with 10 μm in thickness) with another ferroelectric liquid crystal mixture in which the P_s was around 4×10^{-8}C/cm^2. Figure 16 also shows that of 3M2CPOOB.

These results clearly indicate that these new ferroelectric liquid crystals and their mixtures can be practically used in high speed electro-optic devices.

SUMMARY

The results of the present study can be summarized as follows.

1. New ferroelectric liquid crystals with spontaneous polarization exceeding 3×10^{-7}C/cm^2 were prepared using isoleucine, valine, leucine, amylalchol, 2-amino butanoic acid as starting materials.
2. These new materials also exhibited extremely large dielectric constant larger than 7000.

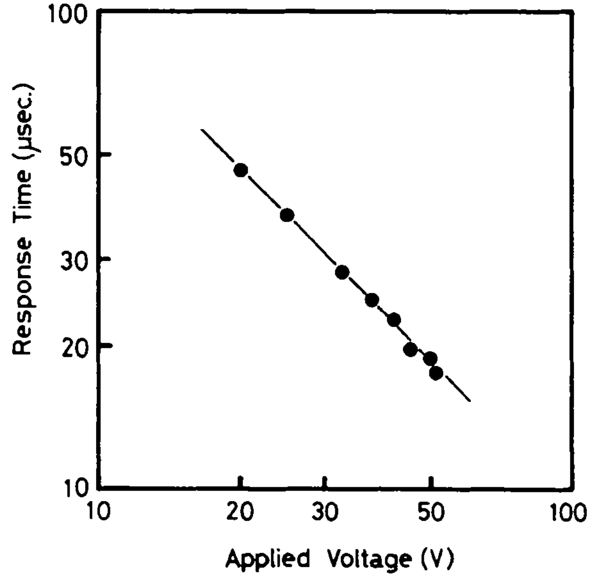


FIGURE 15 Dependence of the response time of the electro-optic cell of type 2 (SSFLC) with a ferroelectric liquid crystal mixture on applied voltage at 27°C.

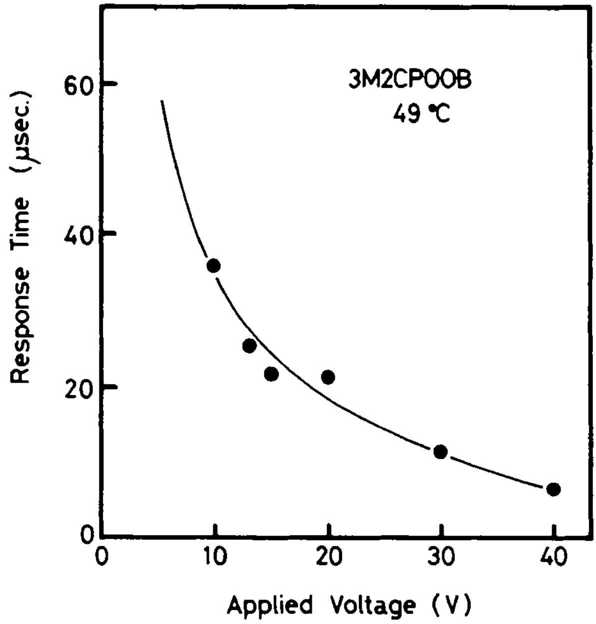


FIGURE 16 Dependence of the response time of the electro-optic cell of type 2 (SSFLC) with 3M2CPOOB on applied voltage.

3. The anomalous dielectric behaviour like the hysteresis in temperature dependence of dielectric constant, was also observed and it was explained in terms of surface effects.

4. These new compounds exhibited novel electro-optic effects.

5. Even the most simple electro-optic effect utilizing the change of the light transmission by the transition between wound and unwound states was found to exhibit very low threshold voltage and high response speed, consistent with the large spontaneous polarization.

6. The response time of SSFLC type cell and TSM type cell was also found to be very short, less than several tens μsec.

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