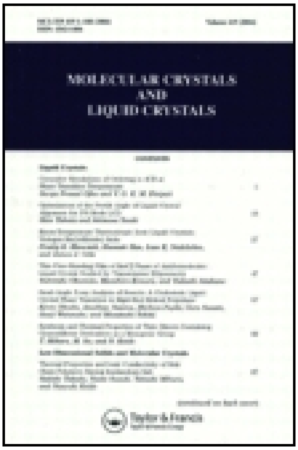

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Electrical and Optical Properties of Ferroelectric Liquid Crystals and Influence of Applied Pressure

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Electrical and Optical Properties of Ferroelectric Liquid Crystals and Influence of Applied Pressure

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Much larger dielectric constants and spontaneous polarizations are evaluated in the smectic-C phase of p-alkoxybenzylidene-p′-amino-2-chloropropyl-cinnamate (HOBACPC, OOBACPC and DOBACPC) which have dipole moments at the chiral part compared with those of p-alkoxybenzylidene-p′-amino-2-methylbutyl-cinnamate. In the mixture of D-DOBAMBC and L-DOBACPC with inverse chirality, the pitch of the helical structure is longer compared with those of original compounds. On the other hand, the dielectric constant and the spontaneous polarization of the compounds are nearly linearly dependent on the concentration of L-DOBACPC.

The phase transition temperature from smectic-A to chiral smectic-C phases in DOBAMBC decreases remarkably with the mixing of organic molecules (PAA, eicosane, etc.) but increases with applied pressure.

The threshold field of electro-optical effects (transmission increase, colour switching, memory effects) in DOBACPC and HOBACPC etc. is lower than that in DOBAMBC etc. in accordance with the increase of the spontaneous polarization in the former.

1 INTRODUCTION

Since the discovery of the ferroelectricity in the chiral smectic-C phase of DOBAMBC,[1] extensive studies have been done mainly on this material.[2–5] The spontaneous polarization of this material was estimated to be much smaller than those in solid ferroelectrics, which was explained in terms of a rotation of a molecule around its long axis and intra-molecular rotation or vibration. Liquid crystal with a larger spontaneous polarization was expected in a molecule in which a dipole moment is located at a chiral part and such a material was synthesized by Keller *et al.*[6] However, detail dielectric properties of this material have not been revealed.

Paper presented at 8th International Liquid Crystal Conference, Kyoto, Japan, June 30–July 4, 1980.

Ferroelectric liquid crystals are considered to be improper ferroelectrics. Namely the hindrance of a free rotation of a molecule around its long axis due to an intermolecular interaction caused by the chirality is considered to be essential for the appearance of ferroelectricity. Therefore the effect of a pressure or the insertion of foreign molecules which should change an inter-molecular interaction is quite interesting.

In this paper we will report the detail dielectric properties of several ferroelectric liquid crystals and their mixtures, and influence of pressure on them. Electro-optical effects in these materials will be also discussed.

2 EXPERIMENTAL

Compounds of the series of D-p-alkoxybenzylidene-p′-amino-2-methylbutyl-cinnamate (D-AOBAMBC) and the series of L-p-alkoxybenzylidene-p′-amino-2-chloropropyl-cinnamate (L-AOBACPC) were synthesized after the method of Leclerq *et al.*[7] and a modified version of the method of Keller *et al.*,[6] which is explained in detail elsewhere.[8,9] Synthesized materials were purified with recrystalization from ethanol solution and also by sublimation and chromatography if necessary. Molecular structures of the compounds synthesized in this study and their abbreviated names are listed in Table 1. The samples were sandwiched between two nesa coated glass plates. The spontaneous polarization and the dielectric constant were measured by a Sawyer–Tower method and a capacitance bridge TR10C (Ando–Denki) respectively. The sample cell was mounted on the heat bath on an optical microscope stage to observe simultaneously with electric measurements.

For the observation of the electro-optical effects, the sample was set in an optical path of He–Ne laser (or W-lamp light through a spectrometer) and the change of the transmission light intensity with applied field was monitored by a photomultiplier.

3 RESULTS AND DISCUSSION

3.1 Dielectric constant and spontaneous polarization

Figure 1 shows temperature dependences of the dielectric constant in D-DOBAMBC and L-DOBACPC measured at 110 Hz. A larger dielectric constant is observed in the smectic-C phase (ferroelectric phase) compared with those in the smectic-A and isotropic phases. The maximum dielectric constant in L-DOBACPC is larger by more than factor of 5 compared with that in D-DOBAMBC. However, the temperature range in which the

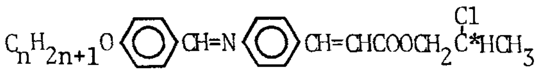
TABLE I

Molecular structures of ferroelectric liquid crystals synthesized in this study and their abbreviated names

D-p-alkoxybenzylidene-p'-amino-2-methylbutyl-cinnamate

n=6: D-HOBAMBC, n=8: D-OOBAMBC , n=10: D-DOBAMBC

n=12: D-DDOBAMBC, n=14:D-TDOBAMBC



L-p-alkoxybenzylidene-p'-amino-2-chloropropyl-cinnamate

n=6:L-HOBACPC, n=8:L-OOBACPC, n=10:L-DOBACPC

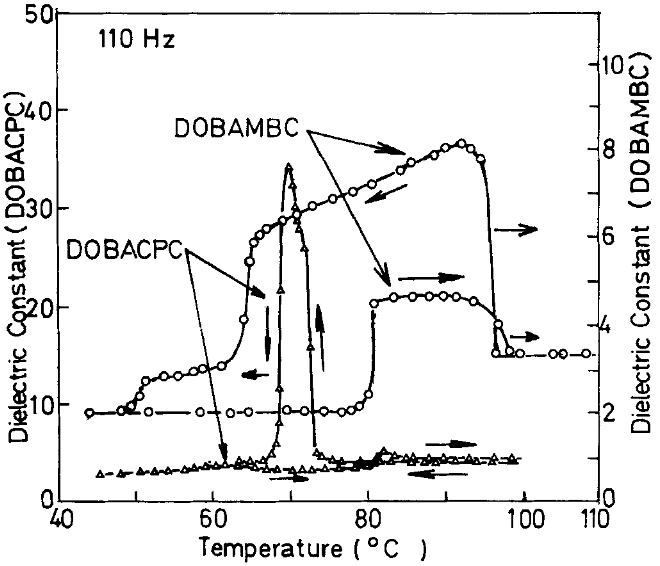


FIGURE 1 Temperature dependences of dielectric constant in D-DOBAMBC and L-DOBACPC measured at 110Hz.

smectic-C phase is observed is much narrower in L-DOBACPC compared with D-DOBAMBC. It should be also noted that in L-DOBACPC the ferroelectric smectic-C phase was observed only in a cooling stage but not in a heating stage (monotropic liquid crystal) contrary to D-DOBAMBC of enatiotropic liquid crystal in which the ferroelectric smectic-C phase was observed both in the heating and cooling stages. Similarly larger dielectric constants are observed in L-OOBACPC than D-OOBAMBC and in L-HOBACPC than D-HOBAMBC. A dispersion of the dielectric constant is observed at higher frequency in AOBAMBC (for example around 300 Hz in D-DOBAMBC) compared with that in AOBACPC (for example around 50–80 Hz in L-DOBACPC). At lower frequencies than this dispersion, extremely large dielectric constant is observed in the smectic-C phase of AOBACPC as shown in Figure 2 for example ($\varepsilon >$ 150 in L-HOBACPC).

It should be also noted that in L-HOBACPC the smectic-C phase was observed both in cooling and heating stages contrary to L-DOBACPC already mentioned.

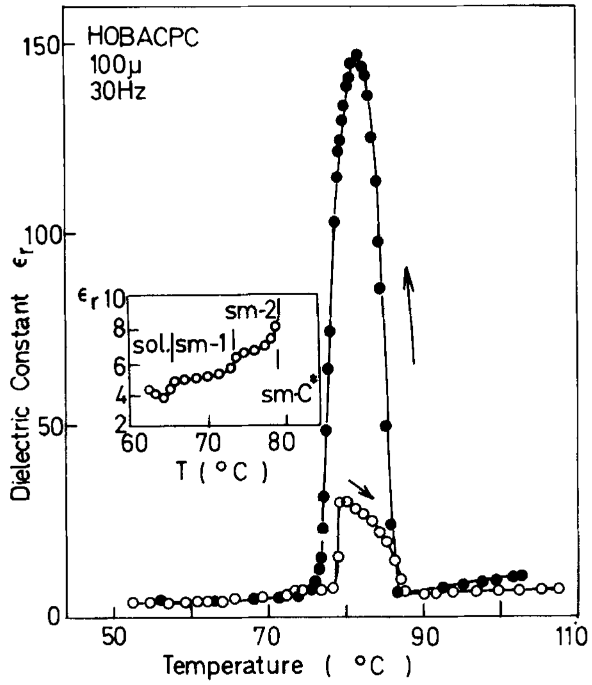


FIGURE 2 Temperature dependence of dielectric constant in L-HOBACPC measured at 30 Hz. Inset: Temperature dependence of dielectric constant around solid-smectic-C phase transition.

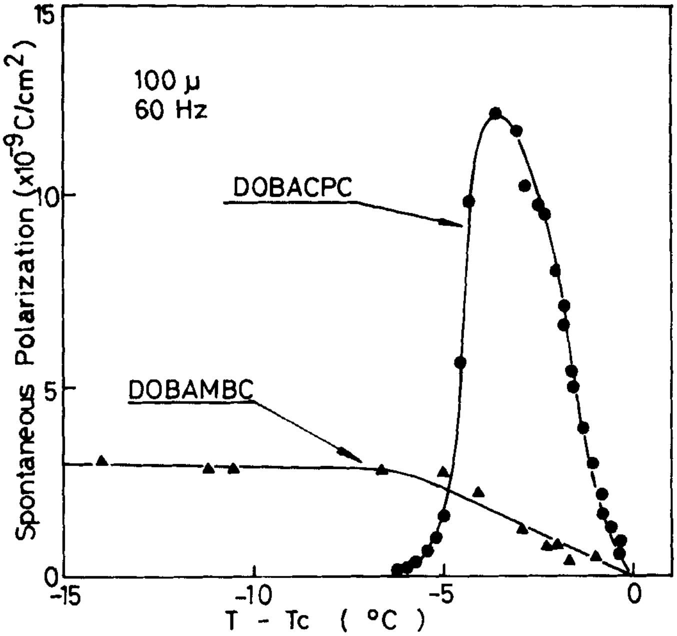


FIGURE 3 Temperature dependences of spontaneous polarization in D-DOBAMBC and L-DOBACPC.

As evident also in Figure 1, the change of the dielectric constant in L-DOBACPC is much remarkable near the phase transition point from the smectic-C to the smectic-A phases than that in D-DOBAMBC.

A D–E hysteresis curve is observed in the smectic-C phase but not in the smectic-A and isotropic phases. Figure 3 shows the temperature dependences of the spontaneous polarization estimated from the D–E hysteresis in L-DOBACPC and D-DOBAMBC. The spontaneous polarization in L-DOBACPC is much larger than that of D-DOBAMBC. As shown in Figure 4, L-HOBACPC also shows larger spontaneous polarization than D-HOBAMBC. Similar results are also observed in L-OOBACPC and D-OOBAMBC.

These facts clearly indicate that ferroelectricity increased by giving dipole moment (chlorine) at the chiral part in AOBACPC, which support the idea that the intramolecular rotation or vibration of a dipole moment relative to the chiral part reduces the spontaneous polarization in DOBAMBC. AOBACPC with longer alkoxy chain indicated larger ferroelectricity. However the temperature range of ferroelectric smectic-C phase is much decreased and the appearance of ferroelectricity becomes critical.

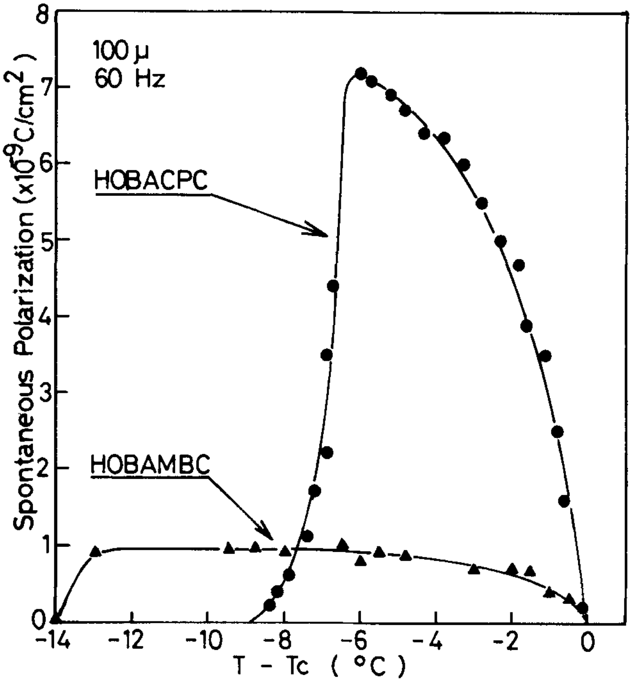


FIGURE 4 Temperature dependences of spontaneous polarization in D-HOBAMBC and L-HOBACPC.

3.2 Properties of mixtures of D-DOBAMBC with PAA and eicosane

Figure 5 shows the temperature dependences of the dielectric constant in the mixtures of D-DOBAMBC with PAA (p-azoxyanisole, nematic liquid crystal) and of D-DOBAMBC with eicosane ($C_{20}H_{42}$). The transition temperatures determined from this dielectric measurement agree with those from an optical observation. The phase diagram of the D-DOBAMBC-PAA mixtures in the low PAA concentration range is shown in Figure 6. Inset is that in the whole concentration range. The transition temperature T_c from smectic-A to chiral smectic-C (ferroelectric) phases which corresponds to a Curie temperature, decreases remarkably with increasing concentration of PAA compared with other transition temperatures (T_{i-sa}: from isotropic liquid to smectic-A, T_{sc-sh}: from smectic-C to smectic-H, and T_{sh-so}: from smectic-H to solid). The distance between parallel stripes which are observed in the optical microscope image with polarized light in the chiral smectic-C phase[10,11] and considered to be originated from helical structure of this

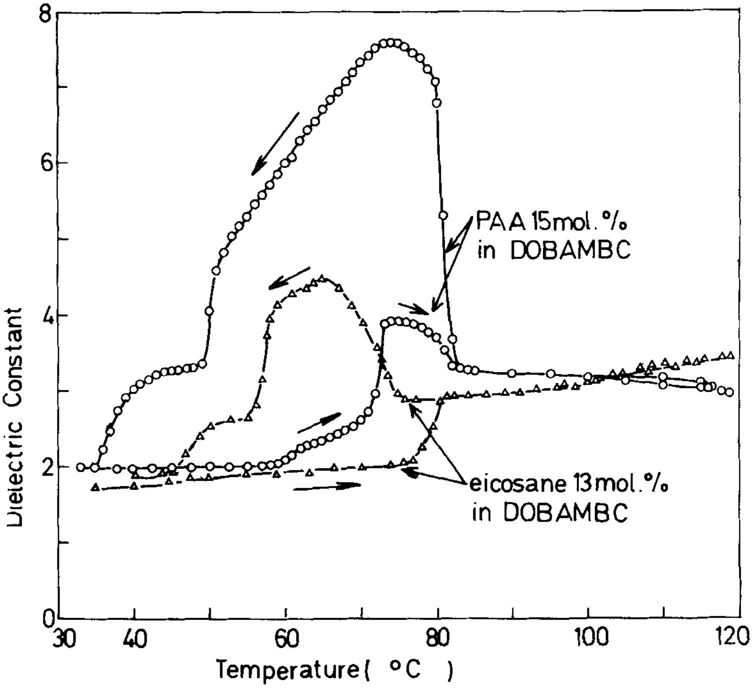


FIGURE 5 Temperature dependences of dielectric constant in D-DOBAMBC-PAA and D-DOBAMBC-eicosane mixtures.

phase, increases with increasing concentration of PAA. The maximum dielectric constant and the spontaneous polarization in the smectic-C phase also decreased by mixing with PAA. These facts indicate that the ferroelectricity decreases in the mixture clearly and disappears at around 25 mol%. The small organic molecules like PAA must enter between D-DOBAMBC molecules and the intermolecular interactions of neighbouring D-DOBAMBC molecules will decrease, resulting in the increased freedom of rotation around a molecular long axis. It is not clear, however, at this stage, whether PAA molecule enters between neighbouring molecules in a layer or between neighbouring layers. Similar effects are also observed in D-DOBAMBC-eicosane mixture as shown in Figure 5. However, in this mixture the stripes observed in the microscope image near T_c is not uniform contrary to the case of D-DOBAMBC-PAA mixture. It should be also noted from Figure 5 for example that in D-DOBAMBC-eicosane mixtures at high eicosane concentration the chiral smectic-C phase appears only in the cooling stage but not in the heating stage. Namely enatiotropic liquid crystal changed to monotropic liquid crystal by this mixing of organic molecule.

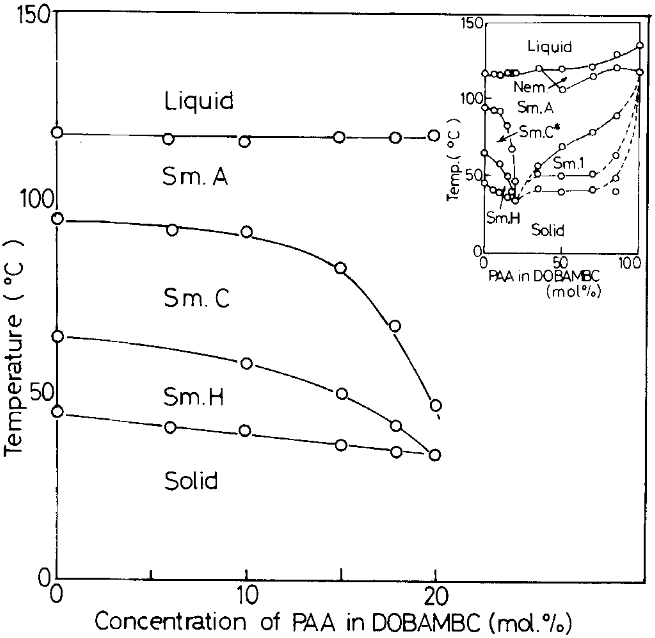


FIGURE 6 Phase diagram of D-DOBAMBC-PAA mixture.

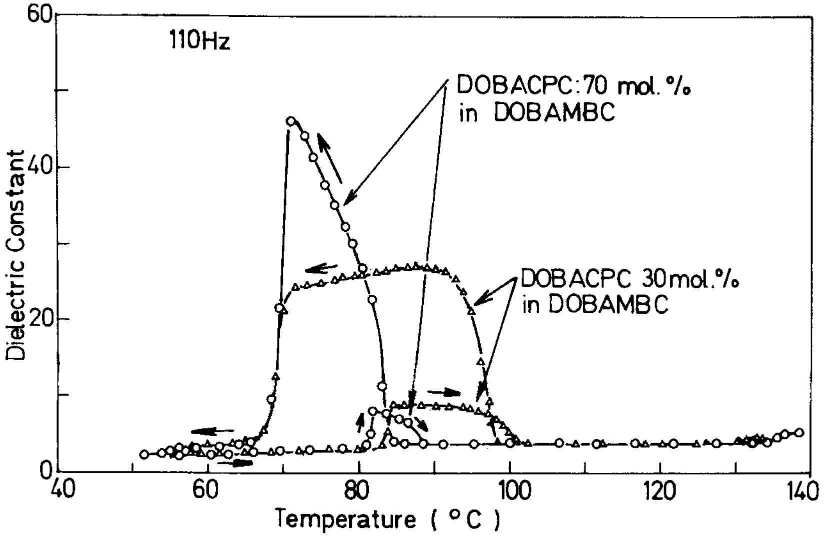


FIGURE 7 Temperature dependence of dielectric constant in D-DOBAMBC—L-DOBACPC mixture.

The understanding of the fundamental physical mechanism of the monotropic liquid crystal is poor compared with enatiotropic liquid crystal at this stage.

3.3 Properties of the mixture of D-DOBAMBC with L-DOBACPC

Figure 7 shows the temperature dependences of the dielectric constant in D-DOBAMBC and L-DOBACPC mixtures of various concentration. As evident from this figure the temperature range of the smectic-C phase becomes wider than that of L-DOBACPC. On the other hand, the dielectric constant in this mixture is much larger than that in D-DOBAMBC. Figure 8 shows the phase diagram of this mixture determined from the measurements of the dielectric constant and an optical observation. It is quite interesting problem to study whether the spontaneous polarization remains in the mixture of the chiral smectic liquid crystals with inverse chiralities and different dipolemoments at the concentration where the helical structure disappears. Though we have not succeeded to remove helical structure completely (pitch → ∞) at this stage in the mixture, we found that distance between parallel stripes corresponding to pitch of the helical structure becomes much

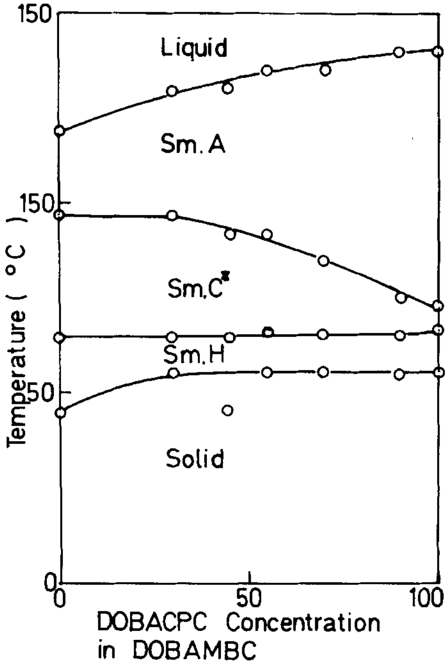


FIGURE 8 Phase diagram of D-DOBAMBC—L-DOBACPC mixture.

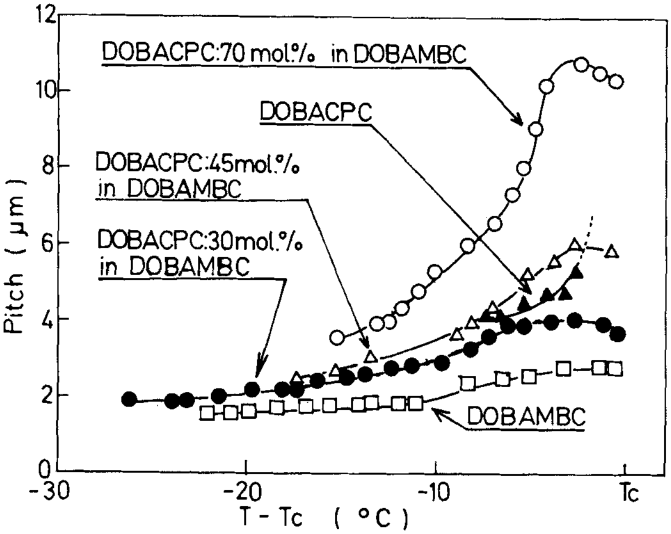


FIGURE 9 Temperature dependences of pitch of helix.

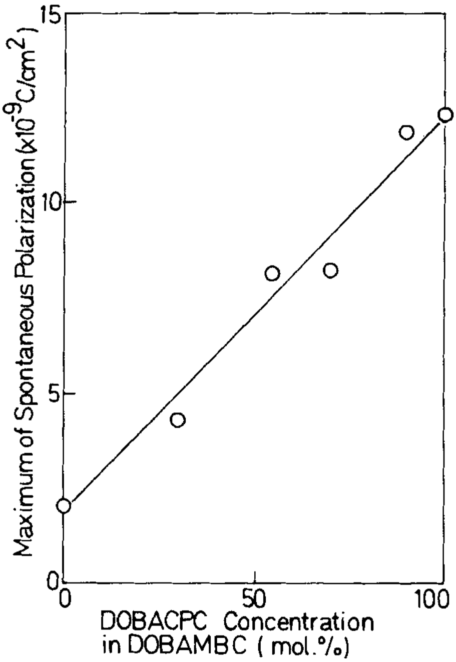


FIGURE 10 Dependence of spontaneous polarization on L-DOBACPC concentration.

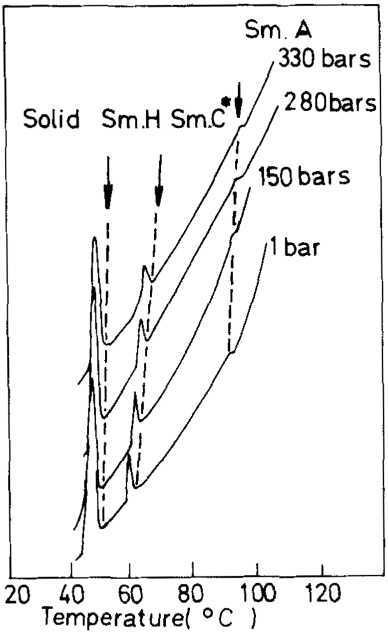


FIGURE 11 DTA curves in D-DOBAMBC under various pressures.

longer at some concentration (around 70 mol% of D-DOBACPC in L-DOBAMBC) compared with original D-DOBAMBC and L-DOBACPC as evident from Figure 9. On the other hand around this concentration the spontaneous polarization is still linearly dependent on L-DOBACPC concentration as shown in Figure 10. These facts seem to support the idea that these chiral smectic liquid crystals are not the anti-ferroelectrics but the ferroelectrics.

3.4 Effects of pressure

Figure 11 shows the DTA curves in DOBAMBC under various pressures. Phase transition temperatures can be defined clearly from these curves. Each peak corresponds to the phase transition temperature of T_c, T_{sc-sh} and T_{sh-so} from higher temperature side respectively. The phase diagram (as a function of pressure) determined from this DTA curves is shown in Figure 12. The phase transition temperature T_c from the smectic-A to the chiral smectic-C phases increases with pressure. However, this temperature dependence is not special for only this transition (Curie point) but all other transition temperatures observed increase similarly with pressure. This

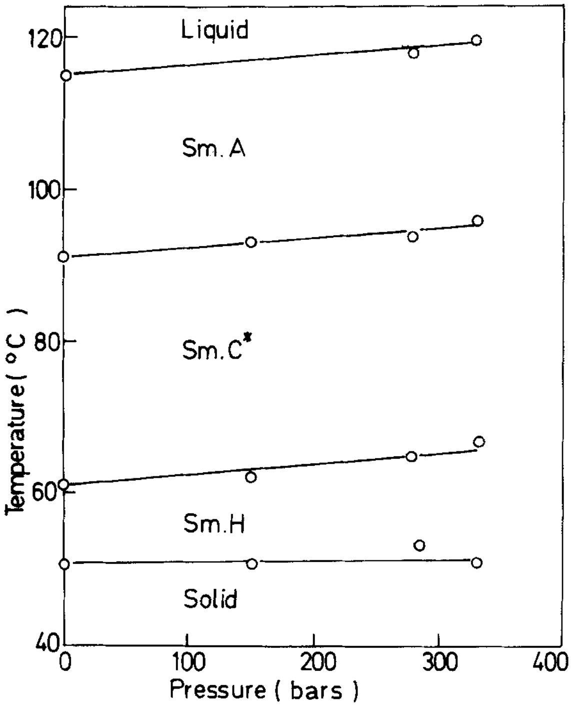


FIGURE 12 Phase diagram of D-DOBAMBC as a function of pressure determined from DTA curves.

shows that under the pressure below 400 bars the ferroelectricity is not influenced strongly. This fact is also confirmed by the observation of pressure insensitive dielectric constant below 400 bars as shown in Figure 13. Studies of pressure effects at the higher pressure range should be necessary and now under progress.

3.5 Electro-optical effects

We have already reported[12,13] the electro-optical effects characteristic for ferroelectric liquid crystals.

1) Transmission of light through homogeneous cell increased by the application of voltage above some threshold. This can be explained in terms of disappearance of helical structure (multi-domain → single domain transformation in some sense), and resulting decrease of the light scattering.

2) Colour switching was also observed by applying voltage on the very thin cell (several μm) of ferroelectric liquid crystals as indicated in Figure 14.

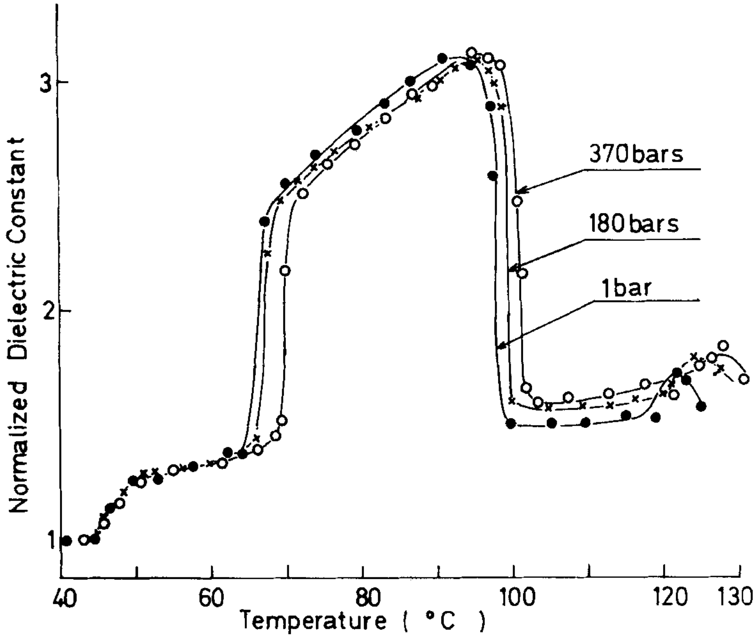


FIGURE 13 Temperature dependence of dielectric constant in D-DOBAMBC under pressure.

This effect seems not to be due to the change of optical rotary power by field application but due to the change of a birefringence on account of the change of the tilt angle of a molecular long axis relative to the normal of the smectic layer, which is confirmed from the transmission spectra as a function of the direction of polarization vector of light as shown in Figure 15.

3) A hysteresis of light transmission was also observed. However, after the removal of applied field, the transmission intensity decreases to original value slowly. This indicates that the monodomain structure relaxes back to the original helical structure slowly due to the relatively low viscosity of liquid crystals contrary to the case of solid ferroelectrics. However, we can use this effect as temporal memory or as a memory by using a small bias voltage.

The electro-optical effects are observed in all ferroelectric liquid crystals and their mixtures. The threshold field for the electro optical effect of (1) in L-HOBACPC is lower than that in D-DOBAMBC as indicated in Figure 16, which corresponds to the increase of the spontaneous polarization in the former compound. The mixtures of ferroelectric liquid crystals have also many advantages for the practical use, because the temperature range of the smectic-C phase can be extended to lower temperatures and also can increase temperature range with maintaining large spontaneous polarization.

SUMMARY

Dielectric properties of ferroelectric liquid crystal of various molecular structures have been studied in detail. Much larger dielectric constants and spontaneous polarizations are evaluated in liquid crystals of L-AOBACPC which have dipole moment at the chiral part than those of D-AOBAMBC. However, the temperature range in which ferroelectricity is observed is much narrower in the former compounds. In the mixture of D-DOBAMBC with L-DOBACPC with inverse chirality the pitch of the helical structure increases compared with those of original compounds. On the other hand, the dielectric constant and the spontaneous polarization of the compounds are linearly dependent on the concentration of L-DOBACPC. These facts indicate that ferroelectric liquid crystal is not an anti-ferroelectric but a ferroelectrics.

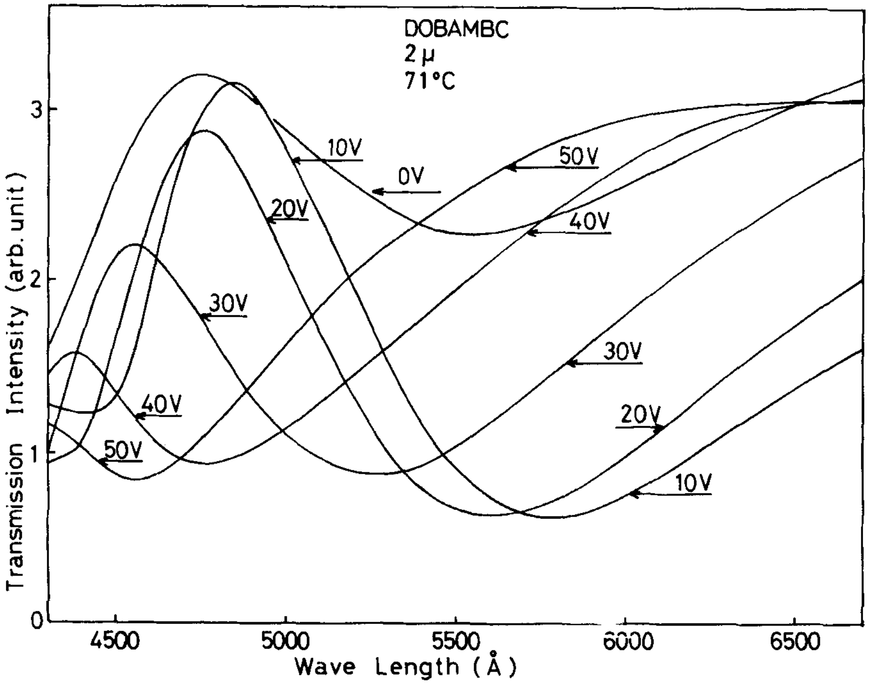


FIGURE 14 Transmission spectra through ferroelectric liquid crystal between crossed nicole under various applied voltage.

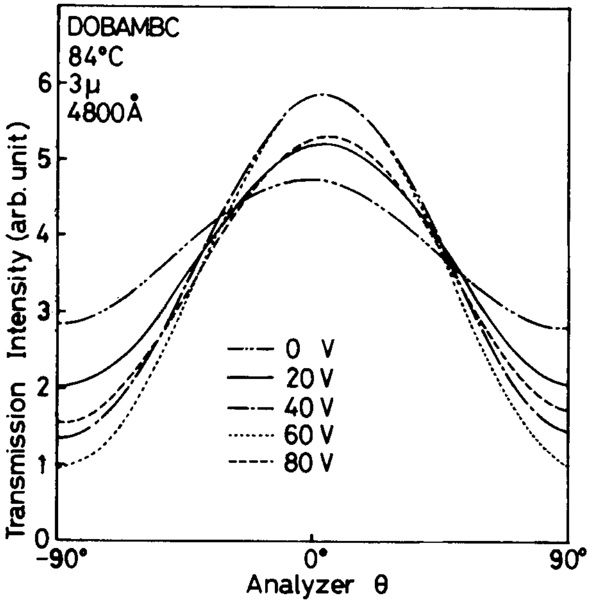


FIGURE 15 Transmission intensity vs. polarization vector of light.

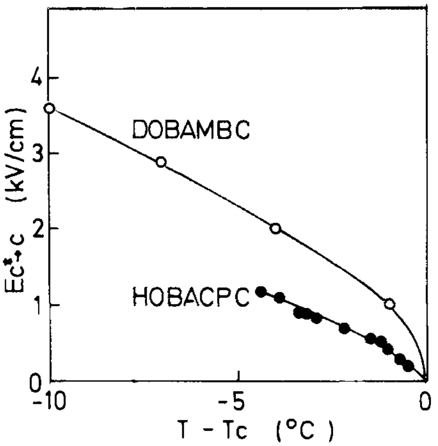


FIGURE 16 Threshold field of electro-optical effect in D-DOBAMBC and L-HOBACPC.

The phase transition temperature from the smectic-A to the chiral smectic-C phases in DOBAMBC decreases remarkably with the mixing of organic molecules (PAA, eicosane etc.) but increase with applied pressure. These results are discussed in terms of intermolecular interaction between DOBAMBC molecules.

Electro-optical effects (transmission increase, colour switching, memory effect) have been observed in these ferroelectric liquid crystals. The threshold field of these effects in AOBACPC (L-DOBACPC, L-HOBACPC etc.) is lower than that in AOBAMBC (D-DOBAMBC etc.) in accordance with the increase of the spontaneous polarization in the former. Mixtures of these ferroelectric liquid crystals also have advantages for the practical applications.

Acknowledgements

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