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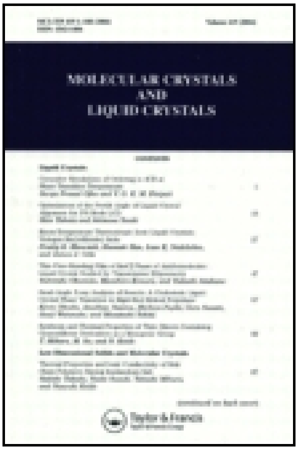

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A Permittive Effect on the Threshold Behavior at Low Frequencies and the Drift of Charge Carriers with a Liquid-Crystalline System of Cyanophenylcyclohexanes

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A Permittive Effect on the Threshold Behavior at Low Frequencies and the Drift of Charge Carriers with a Liquid-Crystalline System of Cyanophenylcyclohexanes

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Measurements are reported for threshold voltage dependence on the frequency of a nematic liquid-crystalline system composed of cyanophenylcyclohexanes (PCHs). The PCH liquid crystals having a strong dipole only at the terminal position of the molecules showed a frequency independent of threshold voltage at low frequencies. In their mixture, increasing permittivity affected the threshold behavior, finally causing a drop in threshold voltage at low frequencies. The difference in systems with and without the drop in threshold voltage was found to be related to the drift of charge carriers. Relaxation time measurements of transmittance against direct current bias revealed a tendency for the drift of charge carriers in the liquid crystal layer. The liquid-crystalline system composed of PCHs showed relatively slower relaxation than the system with increased permittivity due to addition of certain dopants. In the migration of charge carriers, a model is proposed considering the changes of permittivity. In this model the association structure of the liquid crystal molecules is altered by increasing permittivity. Thus the drift of charge carriers, which is related to the formation of interfacial polarization between the liquid crystal and alignment film layers, is promoted by loss of the molecular association structure.

Keywords: nematic liquid crystal, permittivity, threshold behavior, frequency, charge carrier

1. INTRODUCTION

The permittive properties of liquid crystals provide valuable information about assembly behavior and they are significant for most liquid crystal devices. Knowing the intrinsic dielectric anisotropy makes it possible to understand the molecular interactions and orientational order in the liquid-crystalline phase.[1-5] Therefore, it is valuable to relate intermolecular structure and short-range order with the characteristics of liquid crystal devices. So far, materials of positive dielectric an-

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isotropy with longitudinal dipole moments along the major axis of the molecule have been analyzed as showing local antiferroelectric order[6–9] which is considered to be the origin of the relatively weak permittivity dependence on temperature in cyanobiphenyl liquid crystal compounds.[10] The anti-parallel order has also been discussed and thought to affect elastic properties.[11] The results suggest that the elastic constant ratio of bend and splay is affected by such order.

Although no permittive relaxation for liquid crystals or polyimide compounds is usually observed at low frequencies below about 1 kHz, a peculiar drop in threshold voltage is often obtained by combining the liquid crystals with polyimides to form a liquid crystal cell. This behavior seems attributable to an interfacial phenomenon between the liquid crystal and polyimide layers, because it depends on the material combination used in the cell. However, little information has been reported so far on this. Here the effect of liquid crystals on the threshold behavior at low frequencies is reported. At low frequencies, it has been shown that an important factor is the accumulation of space charges near the interface of a liquid crystal with an alignment film due to ionic drift.[12,13] Therefore, relaxation time measurements against a direct current component were carried out to obtain information on the ionic drift in a liquid crystal cell.

In this paper, the doping effect of some liquid crystal compounds on threshold behavior at low frequencies in the liquid-crystalline system composed of cyanophenylcyclohexanes (PCHs) is reported. To understand the difference of the effect of liquid crystal materials on the threshold behavior at low frequencies, an intermolecular structure which is considered to affect the drift of charge carriers is proposed, which considers the permittive properties of the liquid-crystalline system. The proposed model is being used to investigate the threshold behavior, and it may become an important key to understand the behavior of systems with liquid crystals and alignment films at low frequencies.

2. EXPERIMENTAL

Liquid crystal materials (Table I) which show nematic phases at room temperature were used. A mixture (PCHs) of cyanophenylcyclohexanes and cyanobiphenylcyclohexanes components, ZLI-2009 (Merk, Ltd.), was prepared as a base mixture. Liquid crystal compounds, which have a lateral dipole such as ester, alkoxy and lateral fluoro groups were doped into the base mixture. Doping compound was added as 10 mol%.

These nematic liquid crystals can be oriented by a rubbed polyimide surface. The polyimide used in this experiment was composed of 1,2,3,4-cyclobutanetetracarboxylic dianhydride and 1,1,1,3,3,3-hexafluoro-2,2-bis[4-(4-aminophenoxy)phenyl]propane. The thickness of the polyimide was set about 500 Å. Experimental cells for threshold voltage and relaxation time measurements were prepared by sandwiching the liquid crystals between two rubbed films, coated on an indium tin oxide (ITO) glass plate. The plates were set with their rubbing directions twisted by 240 degrees, and the cell gap was fixed at about 6.0 μm.

The threshold voltage measurements were performed by applying sine waves to

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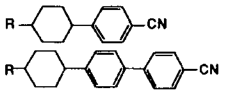
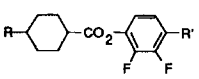
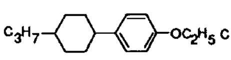
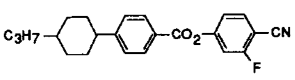
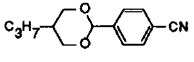
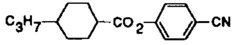
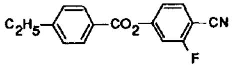
TABLE I

Summary of nematic liquid crystal materials used in this study

Symbol:	•LNG-1	•LTR-1	LTR-2	LTR-3
Main Mixture:		LNG-1	LNG-1	LNG-1
Doping Compound:	—			
Birefringence (Δn):	0.1277	0.1291	0.1220	0.1377
Resistivity ($\rho / 10^{11} \Omega \cdot cm$):	9.39	8.35	2.68	2.59
Dielectric Property(1kHz):				
$\varepsilon_{\parallel}$:	11.13	11.50	11.29	15.56
$\varepsilon_{\perp}$:	3.56	3.94	3.79	4.20
$\Delta\varepsilon$:	7.57	7.56	7.50	11.36

Symbol:	LTR-4	LTR-5	LTR-6
Main Mixture:	LNG-1	LNG-1	LNG-1
Doping Compound:			
Birefringence (Δn):	0.1311	0.1286	0.1286
Resistivity ($\rho / 10^{11} \Omega \cdot cm$):	5.16	12.2	1.91
Dielectric Property(1kHz):			
$\varepsilon_{\parallel}$:	13.41	12.27	16.18
$\varepsilon_{\perp}$:	4.19	4.00	4.69
$\Delta\varepsilon$:	9.22	8.27	11.49

* *R and R' in formula structures symbolize some alkyl groups.*

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the experimental cell so as not to deform the wave form. The transmittance of the experimental cells was measured by a photomultiplier. The threshold voltage was defined as the voltage at 40% transmittance from the black to the white state, and relative threshold voltage, RF, was defined as the ratio of the threshold voltages at 30 Hz and 1 kHz.

Relaxation time measurements against direct current bias were also made by tracing the transmittance of the samples. Applied voltage to the samples was initially set at the threshold voltage, and then 0.2 V biased waves were applied, followed by reversely biased waves. Relaxation time was defined as the necessary time to relax 70% from the transmittance maximum to the initial state.

Permittivity measurements were carried out by preparing homogeneous and homeotropic cells whose thicknesses were set at about 40 μm. Every permittivity was determined by the ratio of the capacitances of the filled cell and empty cell.

Resistivity was calculated from the measured resistance of the liquid crystals using the distance between two electrodes and the area of the electrode. Resistance was measured using a standard apparatus for measuring resistance of liquids. Resistance was obtained by calculating from the applied direct-current voltages and measured current values using Ohm's law.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show two typical cases of permittive behavior of liquid crystals without and with a drop of threshold voltage. With LNG-1 which is composed of liquid crystal molecules having a strong dipole only at the terminal position of the molecule, i.e. a cyano group, no drop in threshold voltage was observed at low frequencies. This corresponded well to the lack of permittive relaxation of the liquid crystal material. The threshold voltage is known to be related to the dielectric anisotropy ($\Delta\varepsilon$) and is proportional to $\Delta\varepsilon^{-1/2}$. The increase of the threshold voltage in the high frequency region corresponded well to permittive relaxation which shows rotational relaxation around a transverse molecular axis. On the other hand, a decrease of threshold voltage with decreasing frequency was observed with LTR-6, which is a mixture of LNG-1 and 4-cyano-3-fluorophenyl-4′-ethylbenzoate, although the permittivity of the liquid crystal was uniform in the same region. The observed drop in relative threshold voltage seemed related to the liquid crystal components.

This interesting behavior could be observed by doping liquid crystal compounds laterally substituted by a strong dipole group or possessing large transverse permittivity into the PCH's liquid-crystalline system. Figure 3 indicates the relation of the relative threshold voltage, as the ratio between 30 Hz and 1 kHz, to the transverse permittivity of liquid crystals. The results explained a tendency for the increasing transverse permittivity to give a nonuniform threshold voltage dependence on frequency, and to have a decrease in threshold voltage. The transverse permittivity could be increased by doping additional compounds laterally substituted by a strong dipole group. But at the same time, these compounds also caused a longitudinal permittivity increase in the system. The relative threshold voltage

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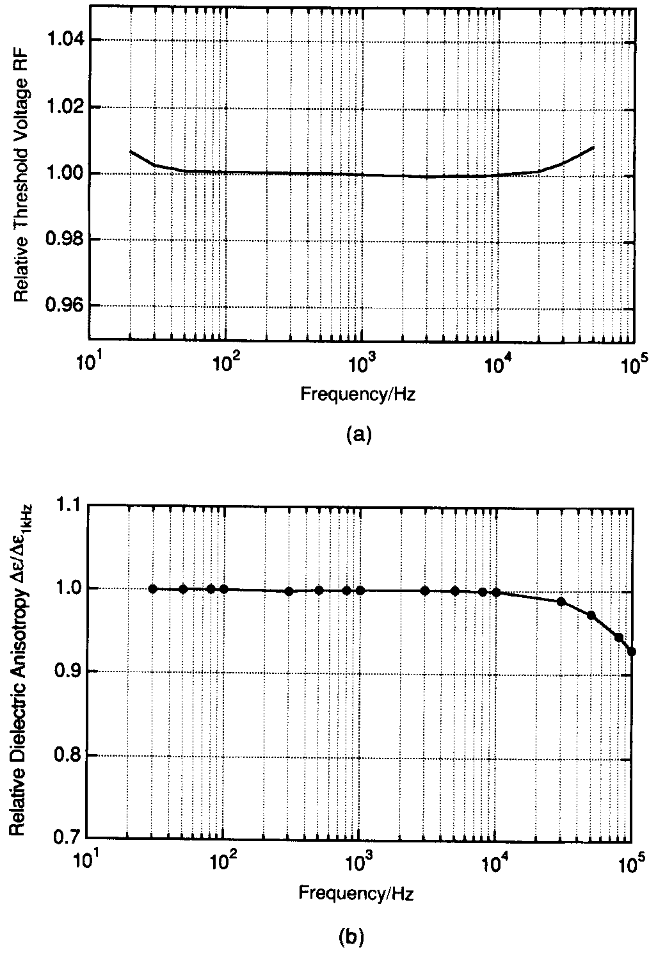

FIGURE 1 Threshold voltage dependence (a), and dielectric anisotropy dependence (b) on frequency for LNG-1.

dependence on the longitudinal permittivity is plotted in Figure 4. As explained in Figure 3, the larger permittivity seemed to decrease the threshold voltage at low frequencies. The effect of each permittivity component on the threshold behavior could not be separated. According to Maier-Meier's theory,[14,15] a larger contribution of lateral fluoro and carbonyl groups to the transverse permittivity should be expected, because the angle between those substituents and the main axis of polarization of the molecule seemed to be larger than 55°. However, dielectric anisotropy was also increased by lateral substituents as shown in Figure 5. This figure plots the relationship of the relative threshold voltage to the dielectric anisotropy. Larger dielectric anisotropy resulted in a lower relative threshold voltage, which implied that longitudinal permittivity contributes more to the threshold behavior at low frequencies than the transverse permittivity does. So this contribution of the doped compounds to the longitudinal permittivity is larger than expected,

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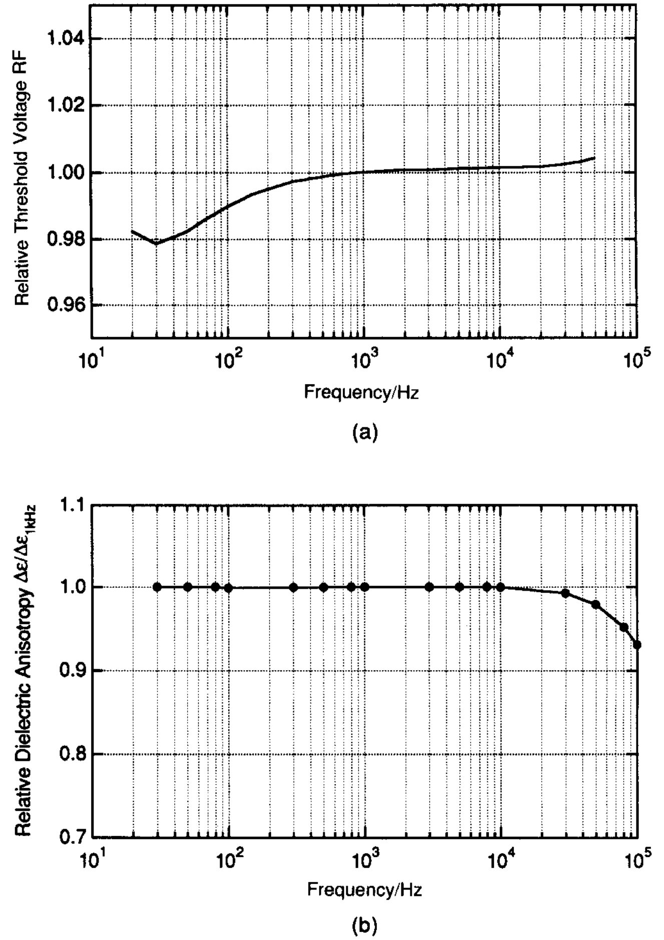

(a)

(b)

FIGURE 2 Threshold voltage dependence (a), and dielectric anisotropy dependence (b) on frequency for LTR-6.

which prompted analysis of the intra- and inter-molecular structures in the system. It may be important to discuss the short-range order or association structures of liquid crystal molecules in the liquid crystals in order to understand the system behavior.

Considering that the drop of the threshold voltage took place at frequencies of less than 500 Hz, surface polarization caused by direct current component was expected to affect the threshold behavior. So, it was thought that charge carriers such as dissolved ions in the liquid crystal layer could affect the threshold behavior. Figure 6 explains the dependence of the relative threshold voltage on the resistivity of the liquid crystals. In spite of the same purification treatment, liquid crystals of large permittivity showed a little lower resistivity compared to those of small permittivity. But all samples indicated at least 10^{11} Ωcm, which, from a theoretical consideration,[16] is not sufficient to affect the threshold behavior. Moreover smaller

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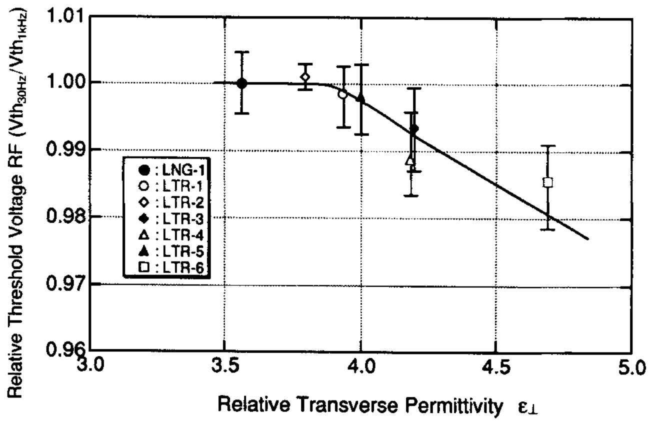

FIGURE 3 Relation between relative threshold voltage at low frequencies and relative transverse permittivity of the liquid crystals.

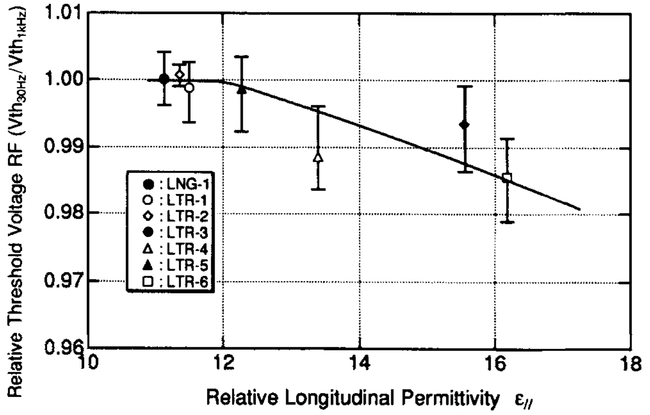

FIGURE 4 Relation between relative threshold voltage at low frequencies and relative longitudinal permittivity of the liquid crystals.

resistivity of the liquid crystal layer can produce a higher threshold voltage. Thus this result suggested that the difference in resistivity could not simply affect the threshold behavior. However, the observed relationship that large permittive liquid crystals tended to decrease the resistivity was also worthy of attention.

To clarify the difference between the charge carriers' mobility in the liquid crystal layer, direct-current biased waves were applied to the liquid crystal cells. Figure 7 shows the applied wave form and the defined relaxation time, and indicates a plausible process for movement of charge carriers. Charge separation is expected to take place in the liquid crystal layer, when the direct current bias is applied to the samples. After this charge separation, each positive and negative ion must be carried toward the interface of the liquid crystal and the polymer alignment film.

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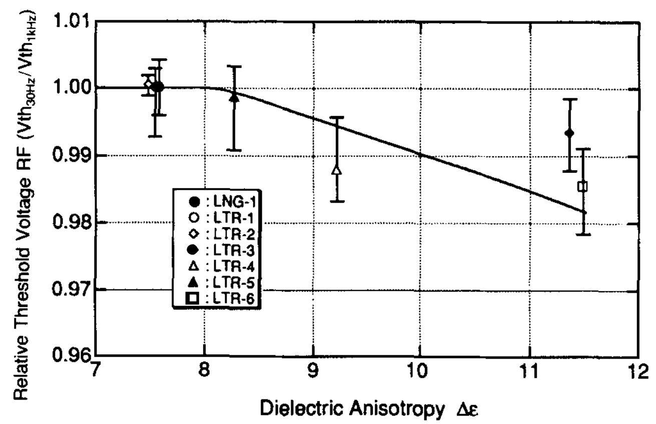

FIGURE 5 Relation between relative threshold voltage at low frequencies and dielectric anisotropy of the liquid crystals.

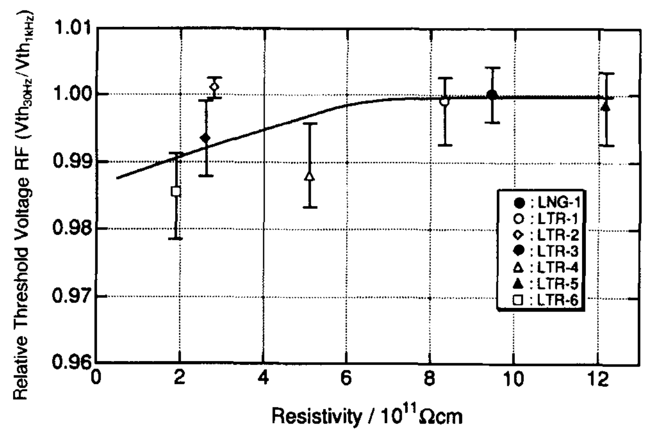

FIGURE 6 Relation between relative threshold voltage at low frequencies and resistivity of the liquid crystals.

At the end of the transport, an electrical double layer must be formed at the interface to neutralize the electric charges on the polymer surface. If a reversed direct current bias is applied, each charge carrier can continue to migrate toward the opposite interface. Relaxation time for this experiment means the time necessary for the charge carriers in the liquid crystal layer, which actively migrate due to the applied electric field, to neutralize the electric charges on the polymer surface. The relation between the relaxation time for direct current bias and the relative threshold voltage is plotted in Figure 8. Apparently systems with no change in threshold voltage dependence on the frequency produced a longer relaxation time, while those with a decrease in the threshold voltage at low frequencies gave a relatively shorter relaxation time. This result easily led to an important finding that

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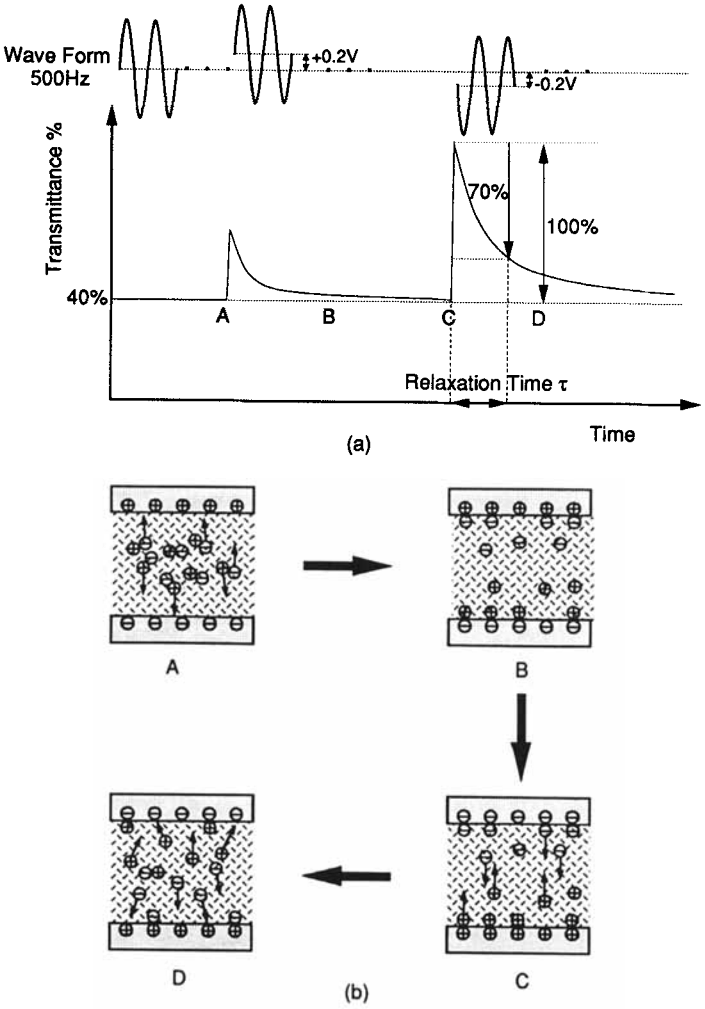

FIGURE 7 (a) Wave form applied to the liquid crystal cell in this experiment and typical response of transmittance against direct current bias, and (b) a plausible process of electric species transportation in the liquid crystal layer with the direct current bias.

the active drift of charge carriers occurred in the system which showed a decrease in the threshold voltage at low frequencies. Consequently, changes in the association structures of the liquid crystal molecules, in which the charge carriers are able to actively migrate, were proposed.

It is well known that a strong dipole-dipole interaction takes place in polar nematic liquid crystals to produce dimer association.[1-9] This associative interaction is pronounced in cyano-substituted compounds. In this study, the base mixture, LNG-1, includes a considerable amount of cyano-substituted compounds. So this system should be described as a monomer-dimer equilibrium. The dimer association constant is related to a correlation factor (g) which is described as $g = (\mu_{eff}/\mu)^2$, using the effective dipole moment (μ_{eff}) and that of an isolated molecule (μ) usually

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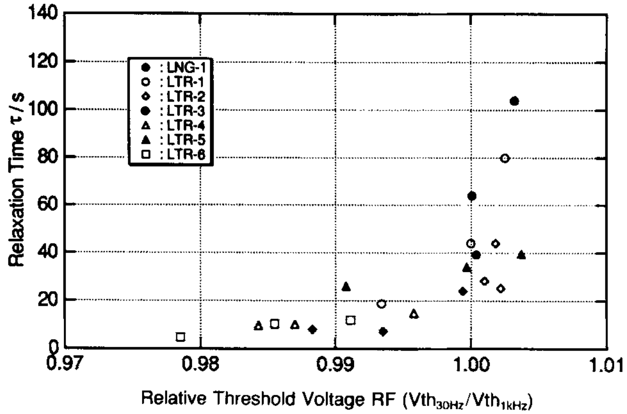

FIGURE 8 Relation between relaxation time against the direct current bias and relative threshold voltage at low frequencies.

obtained from measurements in very dilute solutions.[1] If g equals 1, no dimer association takes place or anti-parallel and parallel dimers are equally formed in the system. With cyano-substituted, i.e. cyanobiphenyl or cyanophenylcyclohexane compounds, the g factor has been found to be as low as 0.4, meaning that anti-parallel dimeric association occurred to a large extent due to anti-parallel dipole-dipole interaction.[3]

In the present experiments, typically monomer and anti-parallel dimer equilibrium could be considered to exist in the base mixture. On the other hand, liquid crystal molecules laterally substituted by a fluoro group next to a terminal cyano group have been found to form parallel dimers to a large extent, which leads to larger permittivity.[3] Reviewing the results in the experiments showed that 4-cyano-3-fluorophenyl-4′-ethylbenzoate in LTR-6 had the most influence on the threshold behavior. 4-cyano-3-fluorophenyl-4′-(*p*-propylcyclohexyl)benzoate in LTR-3 and 2-(4-cyanophenyl)-5-propyl-1,3-dioxane in LTR-4 also caused a decrease of the threshold voltage. These compounds would not be expected to react with liquid crystal molecules in the base mixture. 4-cyano-3-fluorophenyl-4′-ethylbenzoate and 4-cyano-3-fluorophenyl-4′-(*p*-propylcyclohexyl)benzoate typically form parallel dimers. The dimer association constant could be considered as susceptible to the nature of the solvent. It has been found that the dimer association constant of a monomer-dimer system depends on the permittivity even at constant temperature; the dimer association constant of the polar nematic compound cyanophenylcyclohexane has been found to decrease by increasing permittivity.[17] Thus the equilibrium in the base mixture, in which anti-parallel dimers exist, could be changed by the permittive effect. This suggested that the concentration of dimeric species decreased in the base system due to the doping compound in LTR-6, LTR-3 and LTR-4. In a polar medium, the compounds could dissociate into polar monomers. By dissociation of the compounds, the number of liquid crystal monomers would be increased, which might be able to promote the active migration of charge carriers in the liquid crystal layer. Figure 9 shows a plausible model for the relation between dimer association and charge carrier migration. The dimer molecules may possibly

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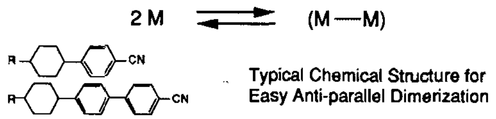
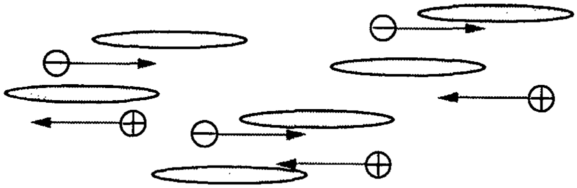
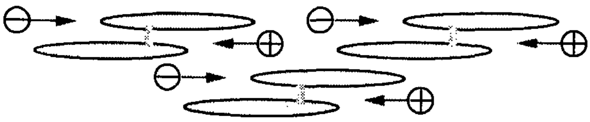


Typical Chemical Structure for Easy Anti-parallel Dimerization



Molecular Structure for Easy Drift of Charge Carriers



Molecular Structure for Difficult Drift of Charge Carriers

FIGURE 9 A possible model considering the relation between inter-molecular structure and charge carrier migration in the liquid crystal layer.

prevent a current flow by the charge carriers. As a result, many charge carriers may be transported toward the interface between the liquid crystal and the alignment film layers to form an electrical double layer. The behavior of this electrical double layer may affect the decrease in the threshold voltage at low frequency, for instance, due to dielectric dispersion of surface polarization.

4. CONCLUSION

A drop of the threshold voltage was observed at low frequencies when doping large permittive compounds into a PCH's liquid-crystalline system which by itself showed no threshold voltage changes in the same frequency region. A tendency for larger permittivity to cause the threshold voltage to decrease at low frequencies was obtained. In the systems where the drop of threshold voltage was observed, active migration of charge carriers was also observed. In the systems where the threshold voltage was frequency independent, limited migration of charge carriers was observed. Considering that the drift of charge carriers is concerned with inter-molecular structure, the large permittive doped compounds could be supposed to affect the polar medium, and promote the dissociation of anti-parallel dimers into monomers. Consequently a model where the charge carriers could easily migrate in the monomeric liquid crystal layer was proposed. As a result, surface polarization formed by the charge carriers may affect the threshold behavior at low frequencies.

To understand the relation of the association structure to the charge carriers' migration, more effort to understand the microscopic inter-molecular structure of liquid crystals is necessary. Moreover further analysis of the relation between the drift of charge carriers and threshold behavior must be made. The effect of an electrical double layer on the threshold behavior is now being investigated.

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