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Ferroelectric Properties of Binary Mixtures of Chiral Smectic C Liquid Crystals

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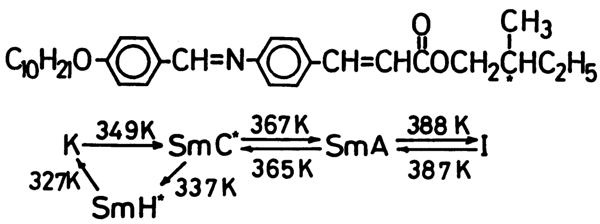
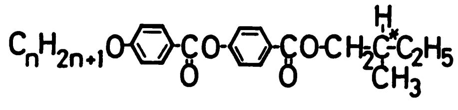
Binary mixtures composed of ferroelectric liquid crystals with various molecular lengthes were prepared. Some of these binary mixtures showed thermodynamically stable ferroelectric phase at around room temperature. The dielectric properties, tilt angles and response times of these mixtures under an imposed electric field were investigated as a function of molecular length of the component liquid crystals. The binary mixture which consists of the liquid crystalline molecules with a similar molecular length exhibited excellent characteristics as ferroelectric liquid crystal for display application.

The ferroelectric chiral smectogens have been paid great attention since they show fast, bistable, electro-optic switching phenomena.[1] The commercial interest takes the focus on the display devices based on the ferroelectric properties of chiral smectic C liquid crystals. However, a number of problems have to be solved before they can be applied practically. One of the most important problems is the development of room temperature ferroelectric liquid crystals (FLC). In the same manner as the development of the twisted nematic device, it is necessary to mix some chiral smectic C liquid crystals to expand the temperature range of ferroelectricity including room temperature.[2] Also, there are other several requirments to obtain the finer display device with a rapid response, such as large spontaneous polarization, appropriate tilt angle, low viscosity for switching and so on. In this report,

4-decyloxybenzylidene-4'-amino 2-methylbutyl cinnamate (DOBAMBC)



4-alkoxybenzoic acid 4'-(2-methylbutoxycarbonyl)phenyl ester (C-n)



n=6,8,10,12,14,16

Fig.1. Chemical structures of constituents for binary mixtures.

the binary mixtures are prepared from FLCs with various molecular length and their phase transitions, dielectric properties, tilt angles and switching speeds have been investigated.

The chemical structures of FLCs used in this work are shown in Fig.1. The 4-decyloxybenzylidene-4'-amino 2-methylbutyl cinnamate (DOBAMBC) is the first ferroelectric liquid crystal reported by R. B. Meyer et al.[3] and used as a standard material by many investigators. However, this liquid crystal is not sufficient for practical application because the temperature range of the chiral smectic C (S_C*) phase (the ferroelectric phase) is 337 K-365 K being fairly higher than a room temperature. The 4-alkoxybenzoic acid 4'-(2-methylbutoxycarbonyl)phenyl ester (C-n) is the ester type chiral material which is chemically stable and colorless. "n" means the number of carbons of the alkyloxy substituent. The phase transition temperatures were determined by differential scanning calorimetry (DSC) measurement and polarizing optical microscopic observation. The variation of the phase transition temperature of C-n with n (n=8,10,12,14,16) is shown in Fig.2. When C-n has the alkoxy group with 8,14,and 16 carbon atoms, the S_C* phase appears near the room temperature. However, the temperature range of the S_C* phase is narrow and this phase is monotropic and thermodynamically unstable because the transition temperature of $S_A \rightarrow S_C$* is lower than the melting point (mp) which is detected as the phase transition temperature of crystal $\rightarrow S_A$ upon heating. Therefore, it is not favorable to aplly C-n independently for practical applications. The binary mixture of DOBAMBC and C-n was prepared in order to expand the temperature range of the stable S_C* phase near a room temperature. The variation of phase transition temperature of these equimolar mixtures of DOBAMBC and C-n

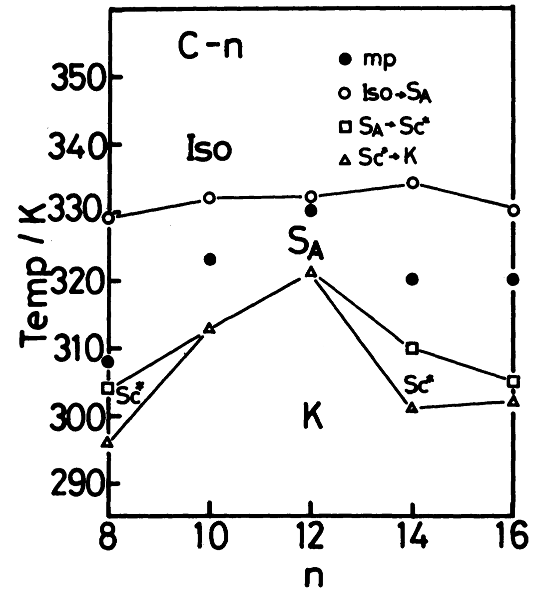


Fig.2. The variation of the phase transition temperature of C-n with the number of carbons of alkyloxy substituent.

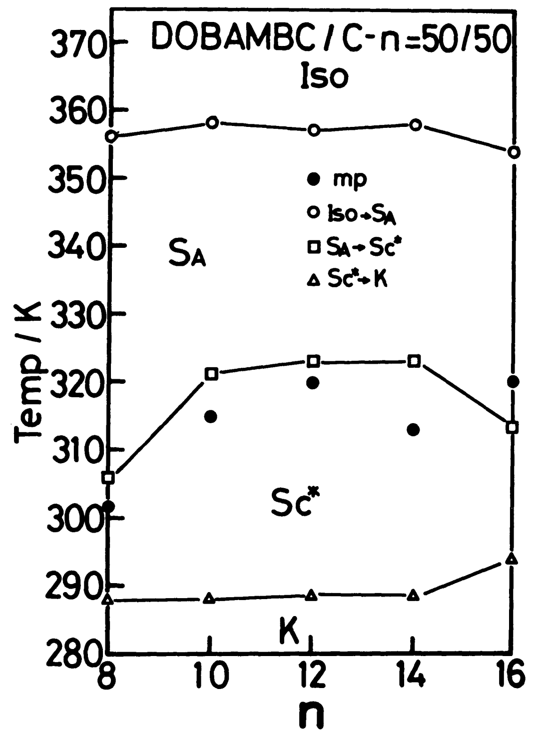


Fig.3. The variation of the phase transition temperature of equimolar mixtures of DOBAMBC and C-n.

is shown in Fig.3. All mixtures exhibit the wider temperature range of the S_C* phase in the vicinity of a room temperature. Except for the mixture of DOBAMBC and C-16, the S_C* phase appears even in the temperature range above mp. This indicates an increase in thermodynamical stability of the ferroelectric state. The characteristic of the ferroelectric phase is greatly improved by binary mixing of DOBAMBC and C-n.

The dielectric constant was measured with the capacitance bridge at the frequency of 100 Hz. The samples were sandwiched between two glass plates on which Al had been evaporated as electrodes, and a Mylar film of 30 μm thick was used as the spacer to fix the cell thickness. Figure 4 shows the temperature dependences of the dielectric constant ε' and the dielectric loss factor ε" for the equimolar mixture of DOBAMBC/C-10. The dielectric constant increased steeply upon cooling down in the vicinity of the $S_A \rightarrow S_C$* phase transition temperature. This means that the spontaneous polarization of the ferroelectric liquid crystal can follow the applied weak ac electric field upon at 100 Hz. Therefore, the dielectric constant increased strikingly because the spontaneous polarization was added to the electric displacement in the liquid crystal due to the phase transition from the paraelectric to the ferroelectric phases. An increment of dielectric constant, Δε' at the point of the $S_A \rightarrow S_C$* phase transition corresponds to the magnitude of the spontaneous polarization. Figure 5 (a) shows the variation of Δε' with the difference in the molecular length between DOBAMBC and C-n for the equimolar mixtures of DOBAMBC/C-n. The molecular lengths were evaluated from the CPK molecular model. The maximum of value appears in the case of n=10 and 12, at which the difference in the molecular length shows the minimum value.

The tilt angle θ of the S_C* phase was evaluated from polarizing optical microscopic observation under electric field. A plot of the magnitudes of θ against the difference in the molecular length are shown in Fig.5(b). The maximum value of θ appears in the case of n=10 and 12 in the similar manner to that of Δε' . Since the magnitude of spontaneous polarization is proportional to sinθ, it is reasonable to consider that Δε' correspondingly depends on the tilt angle. The contrast for the display device which takes advantage of the change in the effective refraction index becomes the maximum when θ is 22.5°.

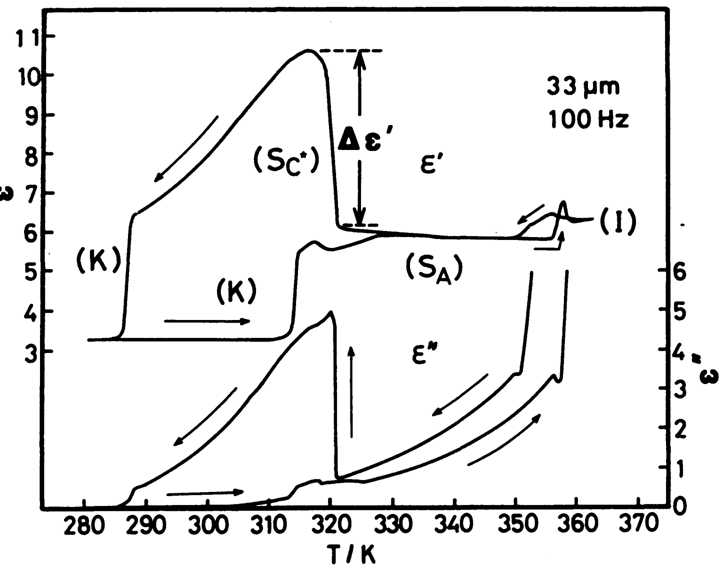


Fig.4. Temperature dependence of dielectric constants for the equimolar mixture of DOBAMBC and C-10 with 33 μm thickness.

The ferroelectric response

time for the molecular realignment to a dc electric field was investigated by the time domain measurement of an electric displacement under a step-function field.[4] The response time, τ was determined from the time at which ∂D/∂logt showed the maximum, where D and t are an electric displacement and the time after an electric field was applied, respectively. The ferroelectric response corresponds to the molecular rearrengement which the helical structure of the S_C* phase is unwound by application of a dc field above some threshold value and turns into the uniform alignment of dipole moment. Figure 5(c) shows the variation of the response time with the difference in the molecular length between DOBAMBC and C-n. The response time becomes the minimum in the case of n=10 and 12 at which Δε' exhibit the maximum. Since the response time is inversely proportional to the magnitude of spontaneous polarization, the response time to an applied electric field is fastest correspondingly to the maximum of Δε' and θ when the molecular lengths of two liquid crystals are almost same.

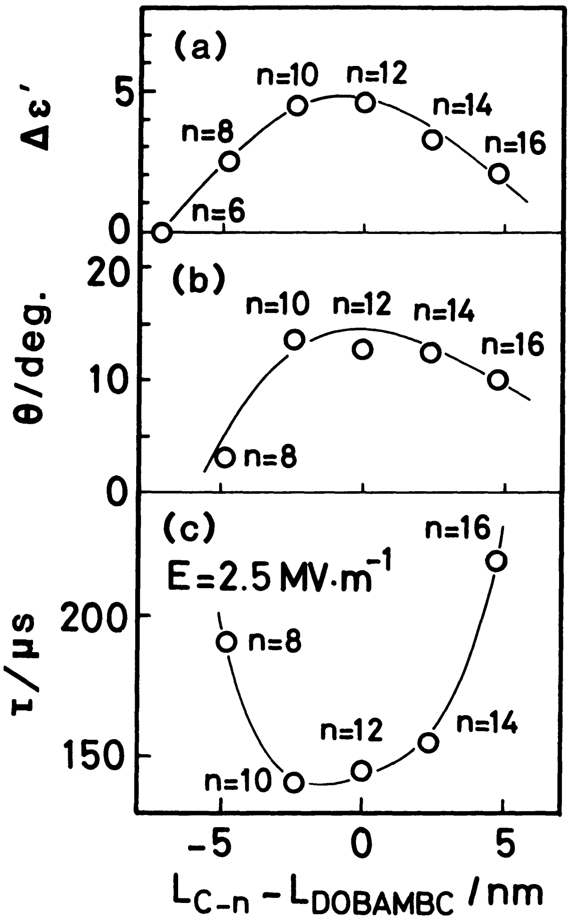


Fig.5. The variations of Δε' (a), tilt angle, θ (b) and ferroelectric response time, τ (c) of the equimolar mixtures of DOBAMBC and C-n at $T-T_c=-3$ K with the difference in the molecular length between DOBAMBC and C-n. T_c is the transition temperature of $S_A \rightarrow S_C$*.

In conclusion, the binary mixture of ferroelectric liquid crystals gives the most appropriate characteristics for the display device when they have similar molecular length. This mixing technique is one of a guiding principle to preparate the thermally stable ferroelectric liquid crystals at room temperature. The aggregation structure-ferroelectric property relationships of this binary mixture will be reported elsewhere.

References

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