Effect of dichroic azo-dye doped on ferroelectric liquid crystals

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In order to study the effect of mixing dye in ferroelectric liquid crystal (FLC) materials, the phase transition temperature and electro-optical properties of azo dye doped FLC samples have been investigated. All the properties have been found to be changed drastically. The results have revealed that not only the SmC*-SmA* transition temperature decreased markedly by the addition of azo-dye, but also dye-doped FLC had lower threshold voltage and saturation voltage than the pure FLC.

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The ferroelectric properties in chiral smectic liquid crystalline phase were first demonstrated by Meyer *et al.* in 1975[1]. Ferroelectric liquid crystals (FLCs) have received high attention of many researchers because of their fast response time and memory effect[2−5]. FLCs have been used widely in electro-optical devices, particularly in display due to their peculiar properties. Most of the studies on FLCs are concentrated around dielectric and optical properties of liquid crystals as these properties are critical for their applications in different devices.

Whenever dye molecules have been introduced into the pure FLCs, their molecular properties changes drastically[6−9]. Some researchers have studied the effect of the addition of dye on the electro-optical behavior of FLCs. Effect of dye doping on dielectric relaxion behavior of FLCs has also been reported by some groups[10,11] as dielectric study provides vital information regarding the molecular interaction of dye and FLC molecules.

Therefore we have concentrated our investigations on the change in transition temperature and electro-optical behavior of FLC materials by the addition of dye. To arrive at a conclusive result, we have investigated one FLC and its mixture with bisazo-dye (3%). We have determined the change in phase transition temperature of pure liquid crystals and dye doped liquid crystals and their electro-optical behavior.

The FLC taken for the present work is FELIX-R2301 (Clariant, Japan). The basic parameters of this FLC are given in Table 1. The structure of bisazo-dye used for present study is given in Fig. 1.

Three dye doped mixtures of FELIX-R2301 were prepared by dispersion of bisazo-dye at concentrations of about 0 and 3% wt.-% ratio in the FLC and we call these mixtures as mixture 1 and mixture 2, respectively. To distribute the dye molecules in the liquid crystals matrix uniformly mixtures have been heated up to the isotropic

transition temperature and agitating the vial containing guest host mixture.

The transparent and highly conducting indium tin oxide (ITO) coated optically flat glass substrates have been used as electrodes. Both the electrodes of the cells have been treated with adhesion promoter (PIA-2720) and rubbed unidirectionally to get planar alignment. The thickness of the cells had been maintained at 2 μm by means of a Mylar spacer. The material has been introduced into the cell by the capillary action at temperature slightly higher than its isotropic one. A well-aligned cell was obtained by applying an electric field in the slow cooling cycle from the isotropic to room temperature. In the present study, three equivalent cells have been prepared, and one of them had been filled with pure FLC and the other two with azo-dye doped FLC mixtures.

The change in phase transition temperature of pure liquid crystals and dye doped liquid crystals was determined by differential scanning calorimetry (DSC). The electro-optical behavior was one of the important properties of FLCs, so we measured the electro-optical behavior of pure liquid crystals and dye doped liquid crystals by liquid crystal display (LCD) parameter tester LCT-5016.

Addition of dye in the pure FLC mixture results in the redistribution of intermolecular interaction energies of pure FLCs. This redistribution of intermolecular interaction energies will result in change in intermolecular interaction of the system, therefore decrease in phase transition temperature was observed. The results has been shown in Fig. 2 and Table 2. Our experimental results revealed that the SmC*-SmA* transition temperature (T_c^*) was decreased markedly by the addition of azo-dye and the T_c^* decreased linearly with increasing dye concentration in Fig. 2. Table 2 shows the phase transition sequence of two mixtures and indicated that the phase transition temperature was decreased markedly by the addition of azo-dye, especially T_c^*.

Table 1. Parameters of Ferroelectric Liquid Crystal

	Phase Transition Sequence	Spontaneous Polarization
FELIX-R2301	I86.1-83.9N*63.4Sc*-2Cryst	3.4 nC/cm^2
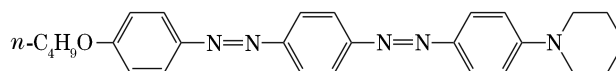
Fig. 1. Molecular structure of the bisazo-dye.

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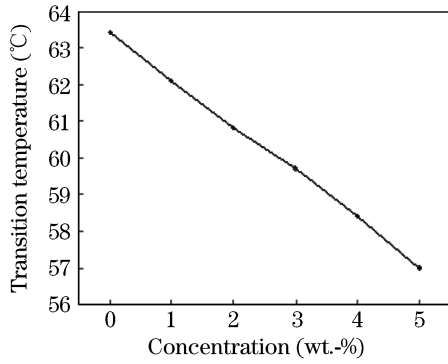
Fig. 2. Dye concentration dependence of N*-Sc* phase transition temperature.

Table 2. Phase Transition Sequence of Two Mixtures

	Phase Transition Sequence
Mixture 1	I 86.1-83.9N*-63.4Sc*-2Cryst
Mixture 2	I 82.4-80.1N*-59.7Sc*

The phenomenon of the decrease of phase transition temperature can be explored by the following theory. In the lowest order, the mean field expression for the nonchiral smectic phase at temperature T can be written as

$$F = F_0 + \frac{1}{2}A(T)\theta^2, \tag{1}$$

where F_0 is the free energy of ground state in smectic A phase, $A(T)$ is the temperature dependent Landau coefficient and may be expressed as $A(T) = a(T - T_c)$, θ is the tilt angle, T_c is the SmC-SmA phase transition temperature. To extend this expression for chiral SmC* phase, we may consider the effect of spontaneous polarization. Therefore the mean field expression for the energy density of chiral molecule may be written as

$$F = F + \frac{1}{2}A(T)\theta^2 + \frac{1}{2}(\chi_P)^{-1}P^2 - CP\theta, \tag{2}$$

where P is the induced polarization, χ_P is the high frequency dielectric susceptibility, C is the electroclinic coupling constant.

When dye is mixed into a pure FLC, the Landau coefficient must be a function of concentration of dye, so $A(T)$ should be replaced by $A(T, x)$. Here x is the concentration of dye in pure FLC mixture. For low orders of T and x, $A(T, x)$ may be expanded as

$$A(T, x) = a(T - T_c) + \lambda_x, \tag{3}$$

where λ is the coefficient of dye concentration. Hence the modified Landau free energy expression for dye doped FLC system may be expressed as

$$F = F_0 + \frac{1}{2}A(T, x)\theta^2 + \frac{1}{2}(\chi_P)^{-1}P^2 - CP\theta. \tag{4}$$

In the equilibrium condition, the free energy will be minimum. Therefore,

$$\frac{\partial F}{\partial P} = 0, \quad \text{or} \quad P = C\chi_P\theta.$$

Hence Eq. (4) becomes

$$F = F_0 + \frac{1}{2}[A(T, x) - C^2\chi_P]\theta^2. \tag{5}$$

Let

$$A^*(T, x) = [A(T, x) - C^2\chi_P], \tag{6}$$

so

$$F = F_0 + \frac{1}{2}A^*(T, x)\theta^2. \tag{7}$$

Equation (7) is similar to Eq. (1), so using these equations we can write $A^*(T, x)$ as

$$a(T - T_{cd}^*) = a(T - T_c) + \lambda_x - C^2\chi_P.$$

Hence the transition point of dye-doped system may be written as

$$T_{cd}^* = T_c + C^2\frac{\chi_P}{a} - \frac{\lambda x}{a}, \tag{8}$$

where T_{cd}^* is SmC* to SmA phase transition temperature of dye-doped system. According to Eq. (3), $A(T, x)$ will be zero at transition temperature, i.e., when x_0, $T_{cd}^* \to T_c$, also T_c^* may be written as

$$T_{cd}^* = T_c + C^2\frac{\chi_P}{a}. \tag{9}$$

Now using Eqs. (8) and (9), we may develop the relation for SmC* to SmA phase transition temperatures of pure FLC and their dye-doped mixture as

$$T_{cd}^x = T_c^* - \frac{\lambda x}{a}. \tag{10}$$

Using the same method, we may develop a similar type of equation for other phase transition temperature of pure and dye-doped FLCs. Thus, the transition temperature is predicted to decrease linearly with the increase of dye concentration.

The electro-optical behaviors of two mixtures are shown in Fig. 3. The curves denote the T-V curve of mixture 1 (pure FLC) and mixture 2 (3% dye-doped FLC), respectively. It shows that they have the same electro-optical behavior, but the dye doped FLC has lower threshold and saturation voltage than pure FLC. The threshold voltage changes from 1.8 to 1.2 V and
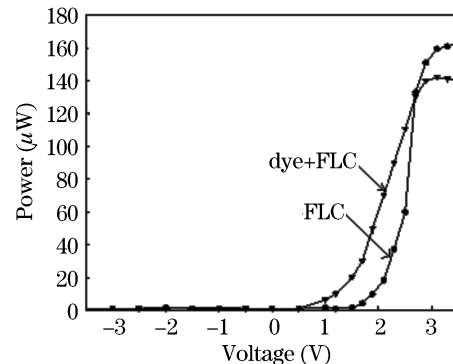

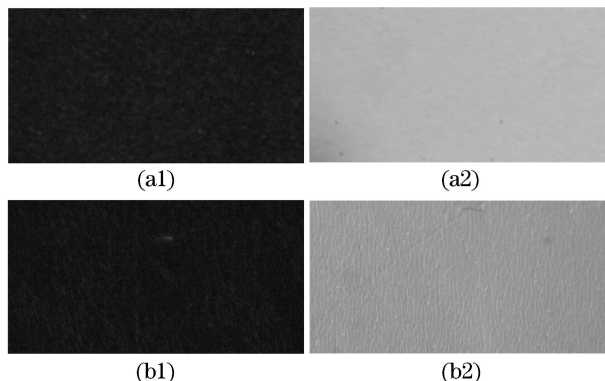Fig. 3. T-V curves of pure FLC and 3% dye-doped FLC mixture.

Fig. 4. Texture of planar aligned pure and dye-doped FLC part.(a1) dark state of prue FLC; (a2) bright state of pure FLC; (b1) dark state of 3% dye-doped FLC; (b2) bright state of 3% dye-doped FLC.

the saturation voltage changes from 3.2 to 2.8 V. The curve gradient becomes slow. This will be favored to actualizing gray-scale and reducing the wastage of polymer network FLCs (NFLCs). It is evident from their texture that the molecular arrangement of dye-doped mixture does not change with the addition of dye but only color change has been observed (Fig. 4). This similarity of electro-optical behavior and the texture suggest that only physical interaction takes place between the molecules of dye and pure FLC mixture.

In conclusion, this letter deals mainly with the effect of dye on the phase transition temperature and electro-optical behavior. The present study can be summarized as follows:

1) The cell doped with 3 wt.-% azo dye shows a completely different phase transition temperature, especially SmC*-SmA*. SmC*-SmA* phase transition temperature shifts towards lower temperature side and this shifting of SmC*-SmA* phase transition temperature has a linear behaviour with concentration of dye.

2) The decrease in phase transition temperature be-

cause the addition of dye in the pure FLC mixture results in the redistribution of intermolecular interaction energies of pure FLCs. This redistribution of intermolecular interaction energies will result in the change in intermolecular interaction of the system.

3) Two mixtures have the same electro-optical behavior, but dye doped FLC has lower threshold voltage and saturation voltage than pure FLC. The threshold voltage changed from 1.8 to 1.2 V and the saturation voltage changed from 3.2 to 2.8 V.

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