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Temperature dependence of physical constants in binary-fluorinated liquid crystal mixtures

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The temperature dependence of dielectric constants and splay elastic constants for fluorinated phenyl bicyclohexane (PBC) binary liquid crystal (LC) mixtures is reported. The results show that the proportions of the constituent elements of binary mixtures strongly influence their anisotropic dielectric constants. For mixtures in which meta-para- and ortho-para-fluorine-substituted molecules are in equal proportion, the effectiveness of the anisotropic dielectric is equal to that with a single para-fluorine-substituted compound. The proportions of a mixture seldom affect the threshold voltage and splay elastic constants in an anti-parallel measurement cell.

Keywords: binary mixture; dielectric constant; fluorine liquid crystal; splay elastic constant; threshold voltage

1. Introduction

Liquid crystals (LCs) have been extensively investigated because they possess properties favourable to applications related to display, tunable photonics and non-linear optics (1). Some of these properties, such as response time, viewing angle, voltage holding ratio, power consumption and operating temperature range, still hold room for improvement, as long as the general LC properties are not negatively affected (2–4). Because specific single LC compounds can achieve the unique desired parameters, LC mixtures have frequently been studied towards this end.

LC materials with high dielectric anisotropy have been realised by introducing fluorine atoms into the compound's structure (5). Fluorinated LCs with such useful characteristics as high electrical resistance, good voltage-holding ratio, tunable polarity, and higher long-term stability have been widely employed. In our previous studies, the temperature properties of some physical constants with varied molecular length and position of fluorine substituents in phenyl bicyclohexane (PBC) LCs were investigated (6, 7). The strong polar effect of fluorine atoms on some PBC LC isomeric compounds has also been investigated theoretically and experimentally (8, 9). For instance, isomeric molecules 3PBC^{2,4}F₂ and 3PBC^{3,4}F₂ possess the same core and fluorine substituents, yet exhibit a marked difference in molecular polarity (7). Detailed information concerning these two binary mixtures remains, as yet, unreported. In this study, we mixed the unitary compound in various weight proportions and studied the temperature dependence of their physical properties.

2. Experimental

The fluorinated PBC LC compounds used in this study have the same 3PBC core structure, but different fluorine substituents on the benzene ring. The molecular structures and phase behaviours of these LCs are shown in Table 1. The phase transition temperatures for LCs are determined by thermal optical microscopy using a polarising microscope (Olympus BH-2) equipped with a hot stage (Mettler FP82). Compared with the unitary fluorinated LC compound, the binary mixtures possess a slightly wider temperature range in the liquid crystalline phase, as shown in Table 1.

The dielectric constant and splay elastic constant were determined from measurements of the capacitance-voltage characteristics. The glass substrates of the capacitance cells were rubbed in anti-parallel directions, with polyvinyl alcohol (PVA) (pretilt angle = 0.2° ~ 0.3°) serving to form a homogeneous alignment layer. A 10- μ m-thick spacer was used in order to maintain an appropriate gap. Since the capacitance of the empty cell and the temperature dependence of thickness were being measured, the cell was filled with LC material in its isotropic phase. An LCR meter (HP4274A) was used in order to measure the capacitance as a function of DC voltage. DC voltages were applied to the cell for 1 s and increased in steps of 0.07 V. Between two successive applications of voltage; an interval of 2 s without DC voltage was required. A low alternating voltage with a frequency of 1 kHz was simultaneously applied to the cell. The resulting measurements were obtained, working from high temperature to low temperature in order to maintain the homogeneous crystal orientation. The cell was set on a hot stage whose temperature was controlled by a thermo-controller (Mettler corp.) with a

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Table 1. Chemical structures and phase transition temperatures.

Structure	Abbreviation	T_{CN} [°C]	T_{NI} [°C]
	3PBC ^{2,4} F ₂	50.4	133.5
	3PBC ^{3,4} F ₂	41.5	120.9
—	3PBC ^{2,4} F ₂ (50 wt%):3PBC ^{3,4} F ₂ (50 wt%)	39.0	128.2
—	3PBC ^{2,4} F ₂ (25 wt%):3PBC ^{3,4} F ₂ (75 wt%)	36.5	125.6
—	3PBC ^{2,4} F ₂ (75 wt%):3PBC ^{3,4} F ₂ (25 wt%)	42.5	131.2

range of accuracy of 0.1°C. The cooling rate was 5°C min⁻¹, with a temperature point that was stabilised in 5 min. The threshold voltage of the anti-parallel cell is described as (8, 10, 11)

$$V_{th,a} = \pi \sqrt{\frac{k_{11}}{\varepsilon_0 \Delta \varepsilon}}, \quad (1)$$

where k_{11} is the splay elastic constant, ε_0 is the permittivity in vacuum and $\Delta \varepsilon$ is the dielectric anisotropy. $\Delta \varepsilon$ is defined as $\Delta \varepsilon = \varepsilon_{//} - \varepsilon_{\perp}$, where $\varepsilon_{//}$ and ε_{\perp} are defined as the long axis and short axis components of the dielectric constant, respectively. The dielectric constant ε_{\perp} was obtained from the capacitance measurements in the absence of voltage applied to the LC cell. The dielectric constant $\varepsilon_{//}$ was obtained from an extrapolation of the capacitance as a function of the inverse voltage, that is, the intercept when the $V_{th,a}/V$ value approaches zero (6). Thus, the splay elastic constant k_{11} can be obtained from Equation (1).

3. Results and discussion

Figure 1 shows the temperature dependence of the threshold voltages in anti-parallel cells, where T is the

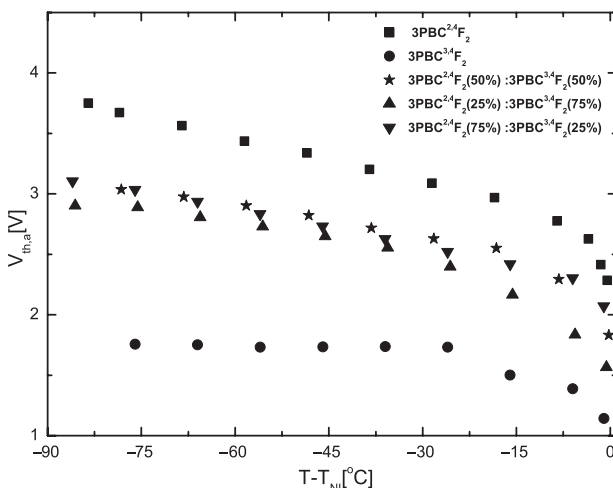


Figure 1. Temperature dependence of the threshold voltage in the anti-parallel cell.

real measured temperature and T_{NI} is the nematic–isotropic transition temperature. A weak temperature dependence for the threshold voltage was observed in compound 3PBC^{3,4}F₂ over a wide range of temperatures. The threshold voltage increases quickly when the cell temperature drops at $T - T_{NI} = -20$ °C. For compound 3PBC^{2,4}F₂, the threshold voltage shows a strong temperature dependence and a value that is higher than those of the other samples. The threshold voltages of the binary mixtures are close to those of the unitary LC compounds. Relative to the meta-fluorine substituent on 3PBC^{3,4}F₂, the ortho-fluorine substituent on 3PBC^{2,4}F₂ produces a higher threshold voltage. The effect of mixing the two on the threshold voltage corresponds to the effect of using a para-fluorine substituted benzene ring, i.e. 3PBC⁴F, as has been reported by Ishikawa *et al.* (see Figure 2 in (11)).

Figure 2 shows the temperature dependences of the dielectric constants $\varepsilon_{//}$ and ε_{\perp} . The variation of the dielectric anisotropy as a function of temperature is shown in Figure 3. The dielectric constants $\varepsilon_{//}$ and ε_{\perp} possess very different temperature dependences. ε_{\perp} fluctuates weakly with temperature, whereas $\varepsilon_{//}$ increases sharply with decreasing temperature. Similarly, the

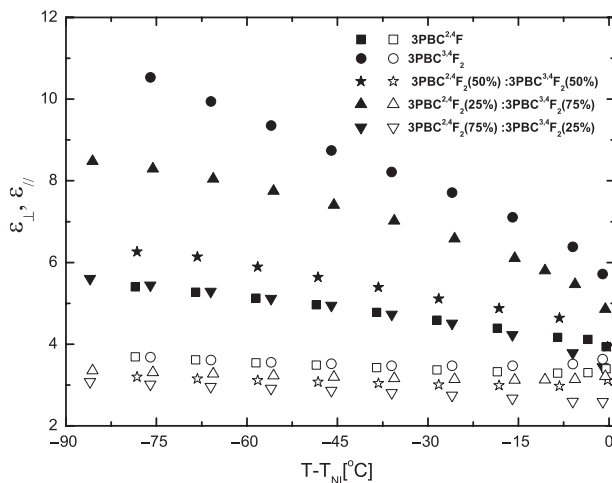


Figure 2. Temperature dependence of the dielectric constant parallel to the long molecular axis (solid symbol) and short axis (open symbol).

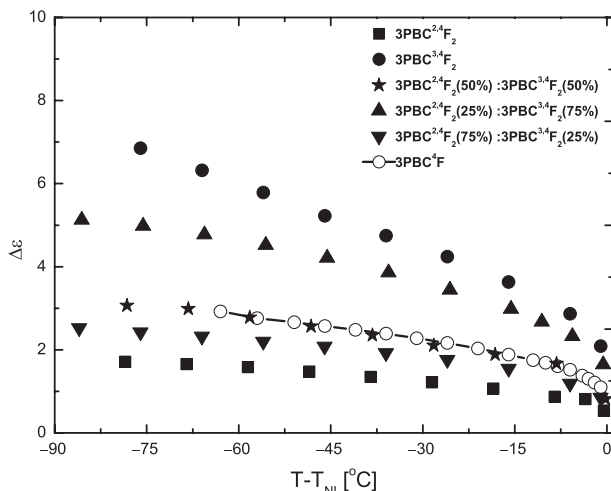


Figure 3. Temperature dependence of the dielectric anisotropy.

dielectric anisotropy $\Delta\epsilon$ shows marked temperature dependence.

Since the carbon–fluorine bond holds a comparatively large dipole moment (1.79 D), it enhances the total molecular dipole moment and contributes significantly to the electric permittivity of the LCs (12). The dielectric constant, which depends on the molecular structure and its dipole moment, has been similarly explained in previous papers (6, 7, 11). By investigating the molecule with a semi-empirical molecular orbital package (MOPAC2002), the calculated dipole moment of 3PBC^{3,4}F₂ (3.230 D) is found to be much larger than that of 3PBC^{2,4}F₂ (1.919 D). It is, therefore, easily understood that the dielectric anisotropy of 3PBC^{3,4}F₂ is greater than that of 3PBC^{2,4}F₂.

We also collected the dielectric anisotropy data on 3PBC⁴F, which has been studied by Ishikawa *et al.* (11) (Figure 3). In this figure, one can see that the proportions of the constituent elements of the mixtures strongly influence their anisotropic dielectric constants. For these mixtures, the illustration of 3PBC^{2,4}F₂ (75%):3PBC^{3,4}F₂ (25%) visibly approaches that of 3PBC^{2,4}F₂ and the illustration of 3PBC^{2,4}F₂ (25%):3PBC^{3,4}F₂ (75%) is clearly close to that of 3PBC^{3,4}F₂.

For mixture 3PBC^{2,4}F₂ (50%):3PBC^{3,4}F₂ (50%), the dielectric anisotropy is not distributed around the mean of the values for 3PBC^{2,4}F₂ and 3PBC^{3,4}F₂, but rather leans towards that of 3PBC^{2,4}F₂. These values are almost equal to those of compound 3PBC⁴F (para-fluorine substituent), which have been reported by Nishi *et al.* (7) and Ishikawa *et al.* (11) (Figure 4 in both references). For a binary nematic mixture comprising structurally similar molecules, the molecular director should be taken along the main axis of the molecular inertia tensor. In other words, each

constituent molecule rotates around its molecular long axis in the mesophase (8). Therefore, as a statistical average of the total transverse dielectric constant, the effects of meta- and ortho-fluorine substitution cancel each other out when the two differently-substituted components are present in equal molecular numbers. Hence, we conclude that the para-fluorine substituent, which is directionally along the molecular long axis, makes the principal contribution to the molecular dielectric anisotropy, more than that made by the meta- and ortho-fluorine substituents.

Figure 4 shows the temperature dependences of the splay elastic constants k_{11} of the samples. Very close values were obtained in the two single compounds and in mixture 3PBC^{2,4}F₂ (75%):3PBC^{3,4}F₂ (25%). For 3PBC^{2,4}F₂ (50%):3PBC^{3,4}F₂ (50%), the value is somewhat greater than that of the component compound. For 3PBC^{2,4}F₂ (25%):3PBC^{3,4}F₂ (75%), k_{11} shows the greatest values. Much research has confirmed that the elastic constants are proportional to the square of the nematic order parameter (6, 13, 14). For 3PBC^{2,4}F₂ (25%):3PBC^{3,4}F₂ (75%) and 3PBC^{2,4}F₂ (50%):3PBC^{3,4}F₂ (50%), the larger splay elastic constant might be due to the mixtures' low T_{NI} and T_{CN} , namely the high-order parameter. 3PBC^{3,4}F₂ has been shown to have great dielectric anisotropy, but low threshold voltage and very little temperature dependence (6, 11). On the contrary, 3PBC^{2,4}F₂ is shown to have little dielectric anisotropy, but a high threshold voltage and great temperature dependence. For the mixtures, one can find that the dielectric anisotropy of 3PBC^{3,4}F₂ makes the principal contribution to the elastic constant, although the threshold voltage of 3PBC^{2,4}F₂ is also a significant factor. Therefore, the

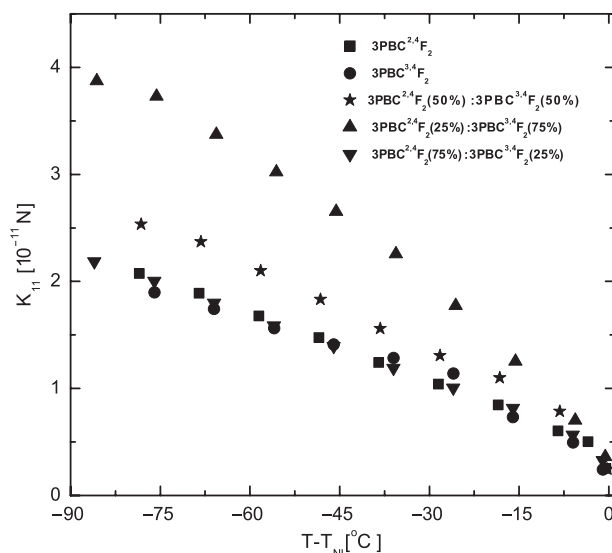


Figure 4. Temperature dependence of the splay elastic constant.

elastic constant of the mixtures expresses itself in a greater value as the contents of 3PBC^{3,4}F₂ are increased. This implies that the molecular properties of association for these two types of unitary materials in the mixture may yet remain obscure (15).

4. Conclusions

The temperature dependences of the threshold voltage, dielectric constant and splay elastic constant for binary fluorinated 3PBC LC mixtures have been noted. The threshold voltage is only slightly different when using binary mixtures. The dielectric properties strongly depend on the positions of the fluorine substituents and the proportions of the mixture. For a mixture with equal proportions of 3PBC^{3,4}F₂ and 3PBC^{2,4}F₂, the effectiveness of the anisotropic dielectric is equal to that with a fluorine substituent on the para-position of the benzene ring. The splay elastic constants have a close relationship to the clear point and melting point, which are in turn determined by the proportions of the constituent elements of binary mixtures.

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