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Dielectric permittivity properties of a fulgide dye guest–host liquid crystal

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The dielectric permittivity of the nematic liquid crystalline mixture E7, doped with a low concentration of the photochromic material thiophene fulgide, was studied and compared with the properties of the pure E7. Fulgides are a group of thermally stable photochromic materials. On irradiation with ultraviolet light, a ring-closure occurs, giving an isomer which is stable if the dye is kept in the dark. The isomerism induces changes to the steric, dipolar and electronic conjugation properties of the species. A capacitive technique was used to determine the dielectric constants of the fulgide-doped liquid crystalline mixtures. The parallel and perpendicular components of dielectric constant were measured using a single cell, in the latter case in the presence of a magnetic field. Measurements were made on the photochromic system before and after ultraviolet irradiation and a marked variation in the dielectric properties of the mixture was observed. This was shown to be entirely due to the differences in phase transition temperatures between the irradiated and non-irradiated guest–host mixtures.

1. Introduction

Substances whose light absorption spectra change markedly on exposure to electro-magnetic radiation, the reverse reaction occurring thermally in the dark or on irradiation at a different wavelength, are said to be photochromic. For organic materials, the forward reaction usually occurs on exposure to ultraviolet (UV) radiation and the reverse reaction can be induced thermally or by using visible light. There are a great many photochromic materials, both synthetic and natural, and much is known about the processes by which they undergo photochromic changes, as is shown by the excellent reviews of the subject [1]. However, the interactions between photochromic species and liquid crystalline materials are as yet less well understood. The work presented here forms part of a detailed study of the physical properties of low molecular weight photochromic liquid crystalline mixtures containing fulgide dyes [2]. These investigations seek to create a better understanding of the interactions of photochromic materials with liquid crystals on a microscopic level by studying the bulk properties of the systems.

In this work the photochromic dye, thiophene fulgide [3], has been dissolved into a nematic liquid crystal at a low concentration to form a photochromic guest–host system. This photochromic species has been used as the guest material as it has new and interesting properties as compared with systems used previously with liquid crystal hosts. As shown in figure 1, the material is cyclized with exposure to UV radiation. The ring-closure process not only brings about steric changes to the photochromic species, but also modifies properties such as the molecular dipole and the electron conjugation within the molecule [4]. Previous work on low molecular weight photochromic nematic [5–7] and smectic [8] guest–host systems has primarily examined azobenzene based materials. Whilst irradiation of such systems produces marked effects, including dramatic changes in birefringence, dielectric constant and spontaneous polarization which are clearly of interest with respect to liquid crystal devices, it is difficult to determine the underlying mechanisms responsible for the effects. The azobenzene materials have a rapid thermal back reaction from the photoisomerized state and so measurements on the irradiated isomer must be carried out

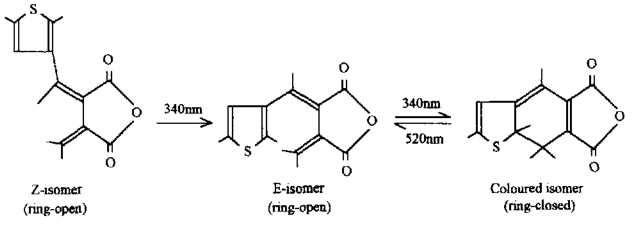

Figure 1. The structure and photochromic changes of thiophene fulgide. The wavelengths of the radiation required to cause photoisomerization are given and two forms of the ring-open isomer are shown.

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under continuous irradiation. This complicates the study of azobenzene based systems as the relative concentration of isomers present is determined by the temperature dependent reaction rates of the isomerization processes. Further, thermal effects due to absorption of the UV light used for continuous irradiation can be difficult to quantify. The azobenzene materials undergo a *cis–trans*-photoisomerism, which brings about a large shape change that often completely destroys the mesomorphic ordering. It is therefore interesting to compare the more subtle photochromic changes of thermally stable fulgide dyes with those of azobenzene materials.

This paper presents the dielectric constants of a guest–host fulgide mixture measured both before and after irradiation of the dye and compares the data with the properties of the host liquid crystal. Measurements are made throughout the nematic ranges of the mixtures. Variation in the dielectric permittivity of the photochromic system on irradiation might be observed due to polarization changes in the bulk system which may be caused by a change in dipole strength, alignment or order parameter. Such phenomena are considered in detail.

2. Experimental

2.1. *Materials*

The nematic liquid crystal host used in these studies was E7 [9], eutectic mixture (for composition see [10]) of biphenyl based liquid crystals, which was used without further purification. This material was designed by Merck Ltd., as a host for bulky dye molecules and was chosen here to allow an acceptable solubility of the guest chromophore. The dye thiophene fulgide was used as the guest material and its structure and photochromic properties are shown in figure 1. The dye undergoes ring-closure when exposed to ultraviolet radiation of wavelength ~ 340 nm, the reverse reaction occurring only on exposure to visible light of wavelength ~ 520 nm. These photochromic properties make the ring-closed form of the dye stable if kept in the dark, i.e. no thermal back reaction occurs under those conditions. Experimentally, this is advantageous, as precise control of the photochromic state of the mixture is possible, and the dynamic effects of the equilibrium state are insignificant compared with azobenzene systems. Two forms of the ring-open isomer occur as shown in figure 1; the Z- and the *E*-form. For samples in the Z-form, initial UV irradiation converts the species to the ring-closed isomer via the *E*-form. However, further photoisomerism occurs only between the *E*-isomer and the ring-closed isomer; only the initial irradiation involves the Z-isomer. The thiophene fulgide material was synthesized specifically for this work at Courtaulds Research Ltd. [11], and it was prepared in its Z-form. A 2% w/w mixture of the thiophene fulgide in E7 was used, referred to here as E7/T2. To distinguish a UV irradiated photochromic mixture containing the ring-closed isomer of the fulgide dye from the non-irradiated, ring-open mixture, an asterisk (*) is used in the text where irradiation has taken place, i.e. the mixture is denoted by E7/T2 before irradiation and by E7/T2* after UV exposure.

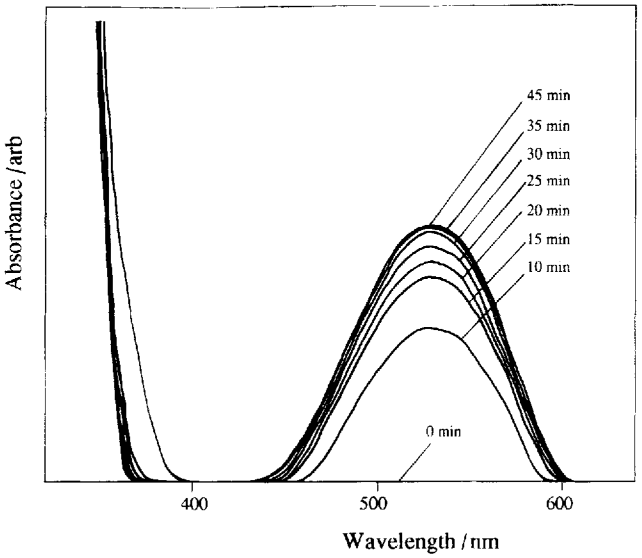

Figure 2. Cumulative absorption spectra for E7/T2 under UV irradiation at 366 nm, where the times are given in minutes. The photostationary state is achieved after 35 min, when further UV exposure no longer changes the absorption profile.

For the ring-closed samples, the photostationary state is found by measuring the successive absorption spectra of the mixture as a function of UV irradiation time for exposure to 4·4 mW cm^{-2} radiation at 366 nm. A Philips Pye Unicam PU8800 UV/Vis Spectrophotometer was used to record the spectra. When further exposure no longer alters the absorption spectrum, the photostationary state was considered to have been reached. This state contains 100 per cent of the ring-closed fulgide (found by NMR studies of the isomers [11]) and has a maximum absorption at around 530 nm, as shown in figure 2. As can be seen from figure 2, the photostationary state is achieved for this set of experimental conditions after 35 min. This final exposure time corresponds to that time necessary for the conversion of the dye from the Z-isomer to the ring-closed isomer.

Molecular modelling of these materials [12] has shown that the *E*-isomer, Z-isomer and coloured form of the thiophene fulgide have molecular dipoles of 5·87 D, 5·72 D and 5·15 D, respectively, and that the biggest change in the relative orientation of the molecular dipole occurs on isomerization between the Z- and the coloured forms of the material. Thus, the influence of the change in molecular dipole moment on the dielectric constants of the mixtures may be expected to be maximized for the photochromic changes between the *Z*- and coloured forms in the materials, remembering that any such contribution will be small at the low concentrations used.

As the thermal back reaction to the ring-open state is negligible on the time-scale of the experiment, it is unnecessary to irradiate the samples continuously once the photostationary state has been reached. Thus, measurements of the ring-closed samples were carried out in the dark, ensuring that any effects which were observed were due to the photochromic changes alone and not to a combination of this with temperature changes caused by the absorption of exciting radiation.

2.2. *Method*

Measurements of the dielectric constants of the materials studied were made using a capacitive technique, in the presence of a strong magnetic field, which follows the method published by Clark *et al.* [13]. Capacitance values of sample cells were determined using a Wayne Kerr capacitance bridge [14] at a frequency of 1 kHz. Cells were constructed as parallel plate capacitors from indium–tin oxide coated glass separated by 50 μm optical fibre spacers with an active area of 0·25 cm^2. A lecithin alignment layer was used to promote bulk homeotropic alignment. Temperature control of samples was achieved using a water circulated sample holder, where a platinum resistance thermometer placed close to the cell allows the temperature to be measured with a relative accuracy of ± 0·1°C. The cells were mounted between the poles of an electromagnet which can produce fields of up to 1·3 T, such that the nematic director was initially normal to the direction of the applied magnetic field.

The dielectric permittivity, $\varepsilon_{\mathrm{meas}}$, of the material filling the cell is determined from the capacitances of the empty and full cell (denoted C_{empty} and C_{full}, respectively). When contributions from stray capacitance at the edges of the electrode area and from lead capacitance (denoted by *X*) are taken into account, the value of $\varepsilon_{\mathrm{meas}}$ is given by [13]

$$\varepsilon_{\mathrm{meas}} = \frac{C_{\mathrm{full}} - X}{C_{\mathrm{empty}} - X}. \qquad (1)$$

For a sufficiently strong magnetic field, *H*, the dielectric permittivity varies due to the nematic director reorientation as [13]

$$\frac{1}{\varepsilon_{\mathrm{meas}}} \propto \frac{1}{H}. \qquad (2)$$

The parallel component of the dielectric anisotropy, $\varepsilon_{\parallel}$, is found directly from $\varepsilon_{\mathrm{meas}}$ at zero magnetic field. The variation of $\varepsilon_{\mathrm{meas}}$ with magnetic field is used to determine the perpendicular component of the dielectric anisotropy, $\varepsilon_{\perp}$, by extrapolation to infinite field ($1/H = 0$) at which a planar configuration would be induced.

The value of *X* was found to be 8·4 pF, whilst capacitance values were determined with an accuracy of ± 0·2 pF. For $\varepsilon_{\mathrm{meas}}$ determined in this way, there is a random error of ± 1 per cent and a systematic error (between different cells) of ± 6 per cent. This results in an error on the measurement of both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of around 6 per cent, although comparisons of dielectric constants made on the same cell (such as for the unirradiated and irradiated photochromic mixtures) would be subject to errors of only 1 per cent.

Dielectric constant measurements were made at a range of temperatures through the nematic phase and into the isotropic phase, where just one permittivity value is observed. Both E7 and the photochromic mixture have a biphasic nematic to isotropic phase transition [2] and so the phase transition is denoted by a temperature range. Within the biphasic region, the measured dielectric constant is difficult to relate to $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, as part of the sample is in the isotropic phase, whilst the rest is in the anisotropic nematic state. The data are scaled with respect to the transition temperatures of the materials. The temperature of the onset of the biphasic region ($T_{\mathrm{N/N+I}}$) was determined by extrapolation for the samples E7/T2 and E7/T2* with an accuracy of ± 0·5°C (see figure 3). $T_{\mathrm{N/N+I}}$ was determined to be 53·7°C for E7/T2 and 55·0°C for E7/T2*. The onset of the biphasic region ($T_{\mathrm{N/N+I}}$) of E7, was determined to be 60·4°C, from the dielectric constant data. The transition temperatures compare well with those determined by polarizing microscopy [2], though it is the transition temperatures found here which are used to determine the reduced temperature dielectric properties of the photochromic mixtures.

3. Results and discussion

The variation of the parallel and perpendicular components of the dielectric constants with temperature for E7, E7/T2 and the irradiated material E7/T2* are shown in figure 3. Curves drawn on the graph are to aid the eye and

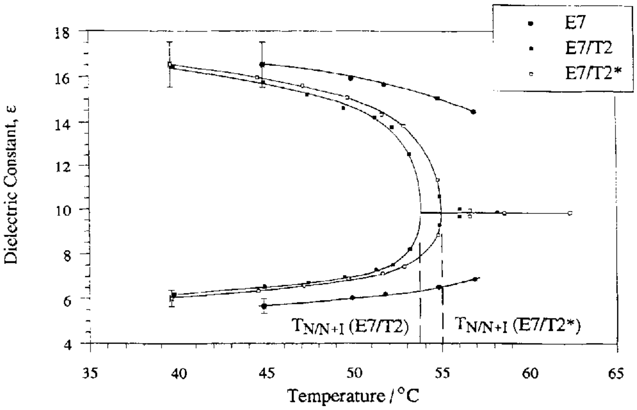

Figure 3. Temperature variation of the dielectric constants of E7, E7/T2 and E7/T2* measured at a frequency of 1 kHz.

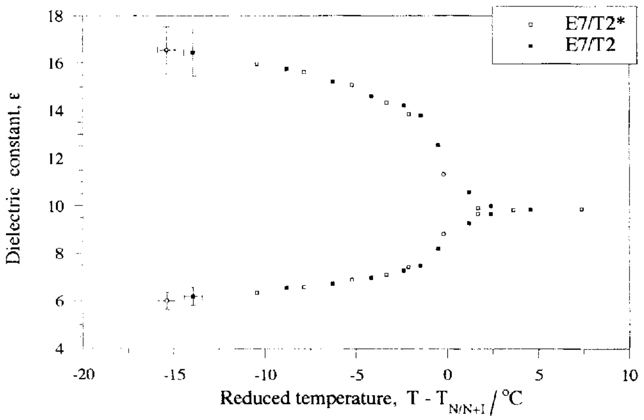

Figure 4. Reduced temperature variation of the dielectric constants of E7/T2 before and after irradiation. Data were measured at a frequency of 1 kHz.

are not a fit to the data. A typical error bar is shown on the graph. Also shown are the values of $T_{N/N+I}$ extrapolated for the mixtures E7/T2 and E7/T2*.

The data show that the addition of the dye to E7 reduces the dielectric anisotropy of the material significantly. There is also a distinct change in the dielectric constants of the guest–host material before (E7/T2) and after (E7/T2*) irradiation of the photochromic dye in the mixture. This change is indicated by the shift of the curve for the E7/T2* up the temperature axis relative to that due to E7/T2. Clearly, a change is observed in the bulk properties of the photochromic liquid crystal system due to the ultraviolet radiation induced changes of the fulgide dopant. The data do not show an abrupt change at the nematic to isotropic transition (as is shown by the curve in figure 3), but vary smoothly towards the isotropic value of the dielectric constant due to the biphasic nature of the materials. A value of each component of the nematic dielectric constant anisotropy measured is averaged with that of the isotropic dielectric constant throughout the biphasic region. Variation of this averaged value occurs as the proportion of nematic liquid crystal present reduces on heating.

Light induced changes in the dielectric anisotropy of photochromic liquid crystal mixtures have been reported previously [5]. It is, however, important to ascribe the effects observed to the appropriate mechanism. The graph in figure 4 shows a reduced temperature plot of the temperature dependence of the dielectric constants E7/T2 and E7/T2*. No differences are observed in the dielectric constants of E7/T2 and E7/T2* at reduced temperatures, indicating that the shift in dielectric constant values shown in figure 3 is due entirely to differences between the phase transition temperatures of the mixtures. Further, when the dyed materials are compared with the host E7 at equivalent reduced temperatures, the data are indistinguishable, i.e. addition of the dye does not change the reduced temperature dielectric properties of the host liquid crystal. It is clear that the dielectric permittivities of the various materials are influenced neither by the differences in dipole moments between the Z- and coloured forms of the fulgide material (which would in any case contribute only ~ 0·4 per cent at the low dye concentrations used) nor indeed by any dipolar contribution due to the presence of the fulgide dye in the liquid crystal host (which might produce ~ 1 per cent difference in the permittivities between the photochromic and pure host materials). These observations are consistent with previous work examining the birefringence and order parameter properties of this fulgide doped system [2].

The changes in dielectric properties of the guest–host system on irradiation are markedly different from those of the azobenzene based mixtures studied by Ikeda *et al.* [5]. That work showed that there was such a disruption to the mesomorphic order on irradiation that the mixture became isotropic at room temperature and the dielectric anisotropy vanished. For the fulgide systems a relatively small change in the dielectric anisotropy is recorded on irradiation. This reflects the differences in geometric conformation of these two photochromic species; the slight shape change of the thiophene fulgide during photoisomerization causes little change in the stability of the surrounding liquid crystalline phase.

4. Conclusions

The photochromic dyes used were initially in the Z-form when added to the liquid crystal. The first UV irradiation of the dyed mixtures induces a change to the ring-closed coloured form of the dye. This is accompanied by the largest shape change possible for the fulgide dye and, consequently, the most dramatic changes in physical properties of the guest–host systems should be seen for this structural change of the dye.

The nematic to isotropic phase transition temperature of the guest–host mixtures was lower than that of pure E7, indicating that the addition of the dye to the nematic host makes the nematic phase less stable. However, the phase transition temperatures of E7/T2* are higher than those of E7/T2, indicating that the ring-closed form disrupts the nematic host less than the Z-form, as might be expected from steric considerations. Further, the irradiated mixture E7/T2* had a larger dielectric anisotropy than the unirradiated E7/T2 at a particular temperature. This was shown to be solely due to the change in transition temperature of the mixture induced by UV irradiation, as the data were identical on a reduced temperature scale. Therefore, there are no dipolar changes to the chromophore that are detectable in the bulk of the mixture on irradiation. From these results it is apparent that the ring-closure of the fulgide species on UV irradiation has no dramatic effect on the structure and ordering of the nematic phase. It indicates that the photo-induced changes of the photochromic material can take place without affecting the liquid crystal host and the systems retain their original physical properties whilst changing their optical transmission properties. The work reported here forms a vital platform for the correct evaluation of more complex systems, such as ferroelectric mixtures.

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