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Perylene-Based Fluorescent Liquid Crystal Dye Guest-Host Mixtures

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We present a study on a series of dye guest-host mixtures using fluorescent perylene-based molecules as the guest dye in an organosiloxane host. These hosts have temperature-independent switching, at room temperature, through 90° for fields of the order of 10 $V_{rms}/\mu m$. Perylene molecules have been grafted onto the organosiloxane moiety via an alkyl spacer producing novel and rugged fluorescent dyes that are readily miscible in the host. Micro-separation of the low molar mass siloxane groups in the mesophases tend to form smectic phases. These planes produce an *effective two-dimensional polymer backbone*that engenders the rugged mechanical properties of polymeric liquid crystals onto these low molar mass ferroelectric liquid crystals. In this study we show how the introduction of the dye molecules affects the electro-optic properties of the organosiloxane host.

Keywords: Ferroelectric; Fluorescent; Organosiloxane; Dye Guest Host

INTRODUCTION

Although FLC Dye Guest Host (DGH) devices are well-established [1-4], dye compatibility and limited solubility have hitherto been a technological problem. Our aim is to produce high solubility dyes that

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more closely mimic the structure of their host. The effect of dye addition is monitored by standard electro-optic measurements of tilt angle, response time and spontaneous polarisation. Crossed polariser optical microscopy and differential scanning calorimetry (DSC) are used to establish phase sequences.

A fluorescent system could be constructed using the dichroic absorption of the fluorophore when exposed to polarised ultraviolet light. However, in addition to this, the selective absorption of the fluorophore to unpolarised UV light could be used to produce a fluorescent device, thus removing the need of a potentially expensive ultraviolet polariser [3]. Fluorescent dye guest-host devices have great potential for display applications due to their inherent brightness above ambient light levels, a far greater contrast and a wide viewing angle of up to 180 degrees [3]. However, due to problems of solubility and degradation of fluorescent dyes in nematics, little work has been done in this area recently. Herein we will describe a perylene dye moiety grafted onto a siloxane group that leads to much higher dye solubility in ferroelectric and antiferroelectric organosiloxanes. We will consider in detail the effect of the siloxane based dye on the transition temperatures, spontaneous polarisation, tilt angle and response times of the ferroelectric siloxane host. The high solubility of the perylene dyes in ferroelectrics should allow a breakthrough in this field, and open up a new range of display technologies.

Host Material

The host materials are members of a family of Low Molar Mass Organosiloxanes (LMMO). Synthesised in house, these LMMOs are based around a central siloxane core and generate ferroelectric or antiferroelectric phases [5,6]. The mesogens consist of a chiral moiety with a laterally substituted halogen, in this case bromine. This is attached to the siloxane end group via a C11 alkyl chain, and denoted Br11-Si3. This monomesogen exhibits a 50°C wide ferroelectric phase, c.f. Figure 3.

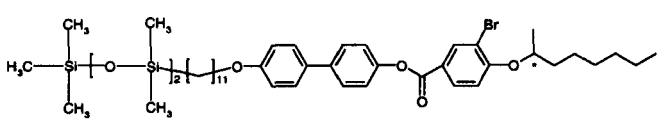

FIGURE 1 Chemical formula of the Br11-Si3 organosiloxane host molecule. * represents the chiral centre.

Guest Dyes

Two dyes have been studied, both based on a fluorescent perylene molecule. The first is a chiral perylene dye [3]. For the second, a single perylene moiety is grafted onto a siloxane core via an alkyl spacer, giving monomesogens that mimic the host shape. This dye is denoted Per11-Si3.

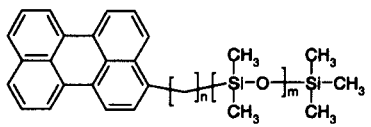

FIGURE 2 Generalised form of LMMO dye molecule with perylene moiety.

Characterisation

In order to assess the physical characteristics of the dyes in a Dye Guest Host environment, we measure the typical characteristics of response time, tilt angle and spontaneous polarisation. The phase sequence and transition temperatures of the mixtures were determined by optical microscopy and DSC. The spontaneous polarisation (Ps) was calculated using the current pulse technique [7]. The response time was measured as the time between the reversal of the direction of an applied square wave and the maximum of the resulting polarisation reversal peak [8]. The samples were analysed in 7μm cells with an anti-parallel rubbed polyamide alignment. They were aligned by cooling just below their isotropic transition and then adjusting the frequency and amplitude of the applied waveform until good alignment was achieved, then cooled into the smectic phase at rates between 0.1 and 0.5 °C per minute.

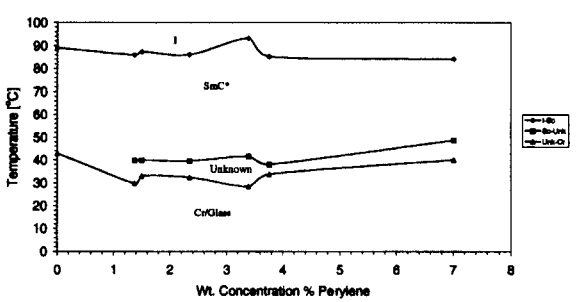

FIGURE 3 Phase diagram for Br11-Si3 with chiral perylene dye addition against w/w concentration.

Mixtures using the chiral perylene dye were made in the range 0-7%, and it could be seen that the dye was hard to mix even at these low concentrations. At 3.4% w/w, the dye already could be seen to crystallise, slowly over days, out of the mixture. The presence of an unknown crystal phase, possibly a pretransitional phenomenon or biphasic regime, was observed in the phase sequence of the mixtures, shown in Figure 3, above.

So far only three mixtures using Per11-Si3 have been made, but they have been found to be significantly easier to mix with the host, i.e. up to 20% by molar weight. Their phase transition temperatures are given in Table 1, below.

Mixture (% Per11-Si3, by mole)	Isotropic-Smectic	Smectic-Crystal
0	89	42.8
2.70	84	38
7.66	85.5	40
20	78.6	33.5

TABLE 1 Phase transition temperatures for the Per11-Si3 dye mixtures in the Br11-Si3 host.

Results

The addition of the chiral perylene dye had little effect on the properties of the host molecule. The tilt angle was still around 45 degrees for fields of the order of 10 V/μm, and the spontaneous polarisation remained around 87 nC/cm^2.

The response times were increased in all the mixtures, and this effect was also observed in the rotational viscosity, which was calculated from the Ps and the response time for fixed field. These can be seen in Figures 4a) and 4b), below.

At these low concentrations, UV absorption spectra taken with a UV-Vis spectrometer did not reveal any fluorescence peaks between 210 and 450 nm, where we would expect to find peaks for a pure perylene mix [9].

Addition of the Per11-Si3 dye had a more pronounced effect. The current pulse response times were slower by around 200μs, but in addition to this the spontaneous polarisation was found to be *higher* for the mixtures over the pure host material. This is shown in Figures 5a) & 5b). Taking the product of these values also showed that the rotational

viscosity was measurably higher. Tilt angle measurements on these mixtures showed a high degree of temperature independence up to the

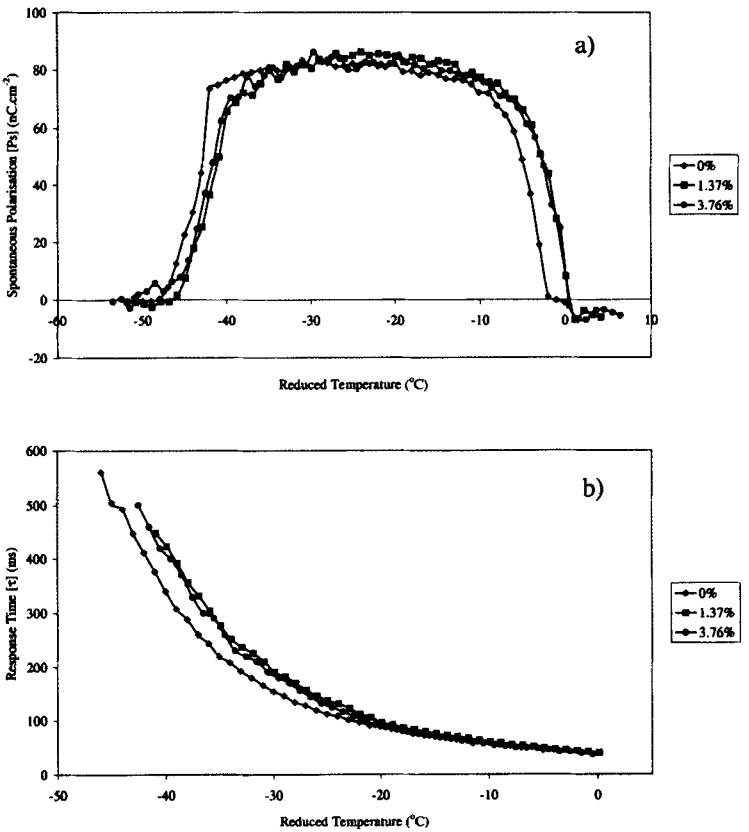

FIGURE 4 a) Typical spontaneous polarisations for the chiral perylene mixes shown at reduced temperature (measured temperature – I/Sc* transition temp.). Measured at ±10 V/μm with a 100Hz triangular field. Percentages are given w/w. b) Typical current pulse response times for the chiral perylene mixtures, measured with a ±10V/μm 100Hz square wave field.

clearing temperature, holding at around 43-44 degrees, over a 45°C temperature range, at fields of the order to 10 V/μm, shown in Figure 6.

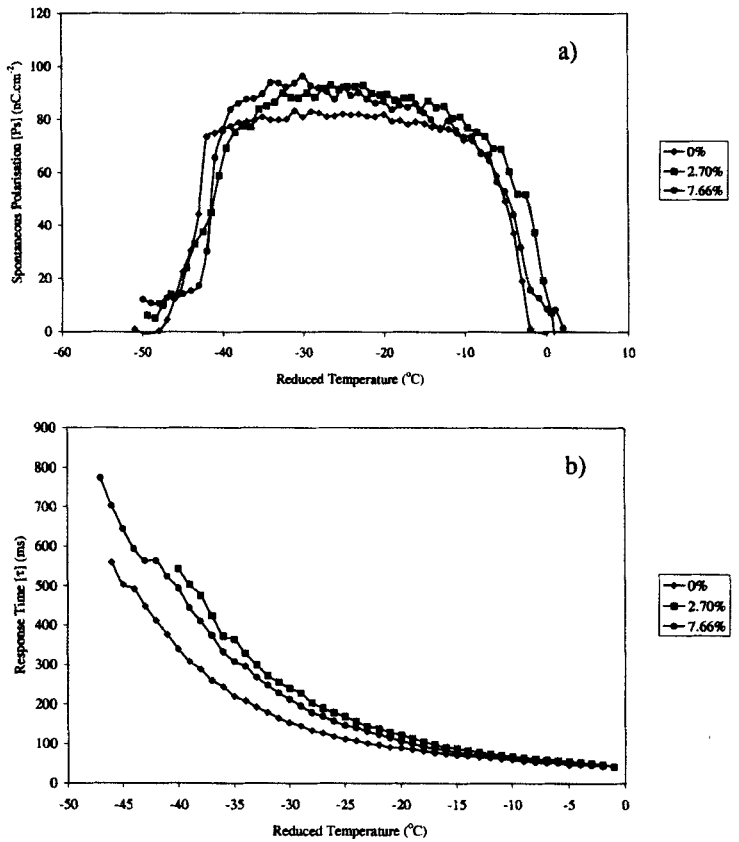

FIGURE 5 a) Spontaneous polarisation for the Per11-Si3 mixes at ±10V/μm shows a marked increase in the Ps. Percentages given are by mole. b) Increased response times for the Per11-Si3 mixtures measured using a ±10V/μm 100Hz square wave field.

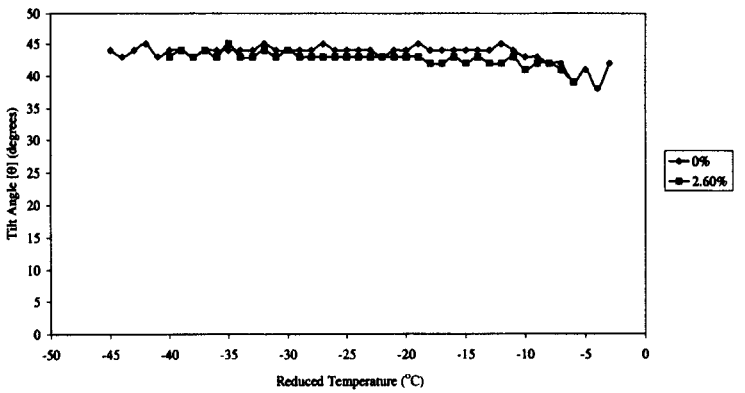

FIGURE 6 Typical tilt angle result of the Per11-Si3 dyed mixture, plotted against reduced temperature. Measured at ±10V/μm 100Hz square wave field.

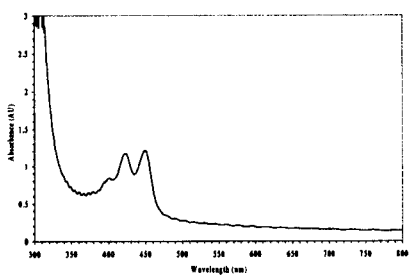

FIGURE 7 Ultraviolet absorbance spectrum of the 7.66% Per11-Si3 mix.

The UV spectra showed definite peaks in the 380-500nm range for both Per11-Si3 mixtures, as would be expected for a pure perylene in solution [9]. This shows that the addition of the siloxane core does not adversely affect the fluorescence of the dye, and at these low molar concentrations the device fluoresces markedly. The intensity of the fluorescent peaks was greatest for 7.66%.

The addition of the siloxane core greatly increases miscibility over the chiral perylene dye. To date we have made stable mixtures with up to 20% molar concentration of Per11-Si3. We are currently examining the electro-optic properties and fluorescent efficiencies, etc. as a function of these high dye concentrations.

CONCLUSION

We have shown that by grafting a perylene molecule onto a siloxane core produces the first successful organosiloxane based fluorescent dyes, thereby making materials suitable for emissive devices. We can create ferroelectric phases with broad temperature invariant properties, i.e. spontaneous polarisation and high tilt angle using these novel materials in organosiloxane hosts.

The organosiloxane based dyes exhibited polarised fluorescence that indicates interesting emissive devices with bistability, fast response and wide viewing angles. It is our hope that these dyes will be the first step in creating new high contrast, bright, low power consumption display technologies.

We are currently carrying out research to optimise the light emissive properties whilst maintaining the advantages of the temperature independent properties and mechanical stability of the "virtual polymer" organosiloxane systems.

ACKNOWLEDGEMENTS

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