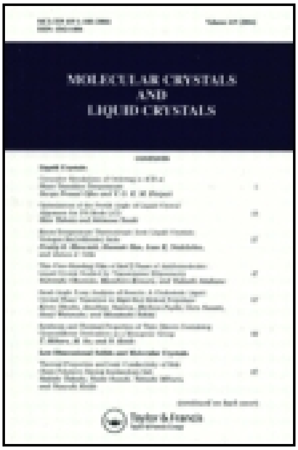

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Low Molar Mass Organosiloxane Liquid Crystalline Dyes for Dye Guest Host Ferroelectric Display Devices

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Low Molar Mass Organosiloxane Liquid Crystalline Dyes for Dye Guest Host Ferroelectric Display Devices

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In low molar mass organosiloxane liquid-crystal materials the siloxane moieties micro-separate and aggregate in planes that could be regarded as an effective or virtual two-dimensional polymer backbone. We show that if a siloxane moiety is attached to a dichroic dye molecule, the micro-segregation of the siloxane moieties makes it possible to include a high concentration of the guest dye (more than 50%) in a host organosiloxane solution. This effect, combined with the temperature independent tilt angles achievable with ferroelectric organosiloxane liquid crystals, provide an ideal material for high-contrast surface-stabilised ferroelectric display devices. We present dyed ferroelectric materials with a temperature independent tilt angle greater than 42 degrees, a wide (room temperature to over 100°C) mesomorphic temperature range and a response time shorter than 500μs in the dye guest host mode.

Keywords: organosiloxane; dye; guest host; ferroelectric

INTRODUCTION

In low molar mass *(LMM)* organosiloxane liquid-crystal *(LC)* materials the molecules usually consist of one or two mesogenic moieties attached via an alkyl chain to a short siloxane group. The materials are mono-dispersed and the siloxane chain contains less than eleven silicon atoms (typically between two and five silicon atoms). In the mesophases, the siloxane groups micro-phase separate from the paraffinic moieties and aggregate in planes that could

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be regarded as a *pseudo* or *effective two-dimensional polymer backbone*[1-4]. This segregation at the molecular level favours the formation of smectic phases and confers to the materials some of the rugged mechanical properties of polymeric LC's. The LMM organosiloxane LC materials are at present extensively investigated not only because of their potential for applications [5-8] but also because of interest from a more fundamental point of view [9,10].

Newton et al [7] have shown that in an organosiloxane LC host the *effective backbone* can be used to introduce a guest material in concentrations far higher than could be achieved by solution. If the guest molecule, not necessarily mesogenic, is also attached to a siloxane group, the siloxanes from the guest and from the host in the smectic phase aggregate in the same layer. The guest moiety thus behaves in the same way as a pendant group on a side chain polymer liquid crystal and its concentration can be significantly increased. This has been called *the effective* or *virtual backbone effect*. The obvious advantage is that "grafting" on the backbone is achieved by simple mixing of the materials. In the present paper we show how this effect can be applied to dye guest host materials for ferroelectric display applications.

THE GUEST MATERIALS

Two series of organosiloxane dyes based on well-known dichroic/fluorescent molecules, the 4-hydroxy-4'-nitrostilbene and an azo dye have been synthesised. In the present paper we describe only the organosiloxane nitrostilbene which is both dichroic and fluorescent; a more complete description of the organosiloxane dyes and their applications in display devices will be given elsewhere.

The organosiloxane nitrostilbene molecule presented here contains three silicon atoms in the siloxane group and eleven carbon atoms in the alkyl chain spacer. A schematic diagram of the molecular structure is shown in figure 1.

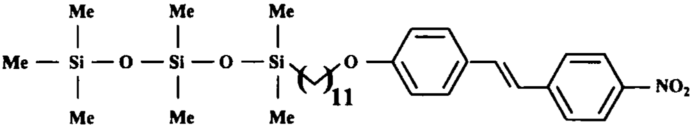

FIGURE 1. A schematic of the organosiloxane nitrostilbene molecule.

Although the 4-hydroxy-4'-nitrostilbene dye moiety has no liquid crystal phases before attachment to the siloxane group, the organosiloxane derivative shown is liquid-crystalline above room temperature. It displays a smectic A phase and a smectic C phase.

The phase sequence determined by differential scanning calorimetry and polarised light microscopy is given in table 1. There is no heat of transition associated with the SmA / SmC transition. The behaviour of the tilt angle as a function of reduced temperature measured with a polarised light microscope is shown later in figure 4. The tilt angle varies rapidly at temperatures close to the SmA / SmC transition and then remains constant at 35 degrees over the rest of the temperature range of the SmC phase.

The optical spectroscopic properties of the nitrostilbene are not significantly affected by the grafting of the siloxane moiety. In figure 2 the optical absorption spectrum of the siloxane nitrostilbene is compared to that of the 4-hydroxy-4'-nitrostilbene. Both spectra were obtained from a dilute solution (0.5% w/w) in dichloromethane using a HP UV-Vis spectrograph.

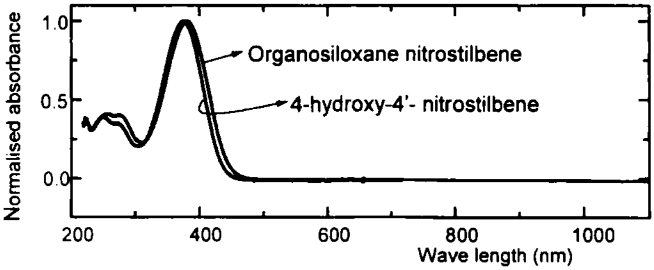

FIGURE 2. The absorption spectra of the siloxane nitrostilbene and the 4-hydroxy-4'- nitrostilbene

THE GUEST-HOST MIXTURES

The Host Material

Our contact preparations indicate that the siloxane nitrostilbene dye is miscible at any concentration with the biphenyl benzoate organosiloxane materials recently discovered to give ferroelectric and antiferroelectric phases[12,13]. The molecular configuration is shown schematically in figure 3.

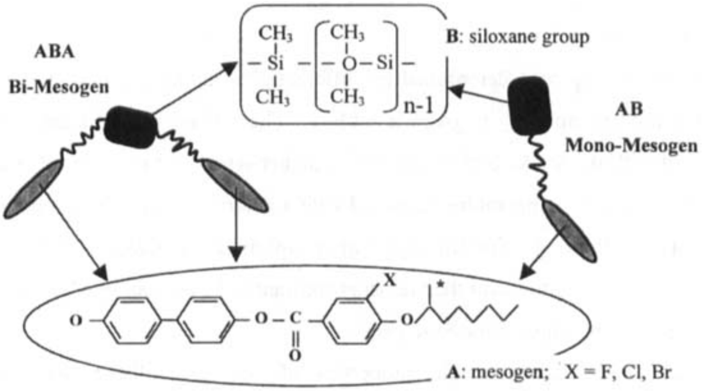

FIGURE 3. A schematic of the molecular structure of the host materials.

The AB and ABA molecules are labelled, respectively, Xm-Si_n and Xm-Si_n-mX where X refers to the laterally substituted halogen, m and n refer respectively to the number of carbon atoms in the alkyl chain spacer and to the number of silicon atoms. The AB materials are all ferroelectric with a temperature independent tilt angle close to 45 degrees. The ABA materials with three silicon atoms are antiferroelectric with tilt angles close to 45° [12].

The Mixtures

We have established[9,11-13] that the characteristics of organosiloxane liquid crystals are to a large extent determined by the conformation of the siloxane group. The conformation adopted by the siloxane in the smectic phase is the one with the lowest energy that is compatible with the packing requirements of the mesogens. In binary mixtures of materials with different packing requirements that conformation can be a function of the concentration of one of the constituents[9]. This appears to be the case with the present materials where the hosts have a conformation that stabilises a 45 degree tilt whereas the guest dye has a conformation that stabilises a 35 degree tilt.

Mixtures with Br11-Si$_3$

The siloxane dye is miscible in all concentrations in the ferroelectric Br11-Si$_3$ material. The temperature range of the mesophase in the mixtures is significantly greater than that in the pure materials; some mixtures are ferroelectric at room temperature. We have characterised two mixtures containing respectively 36% and 16% w/w of the siloxane nitrostilbene dye. A summary of the characteristics is given in table 1; the temperature dependence of the tilt angle is shown in figure 4. At 16% w/w concentration the dye adopts

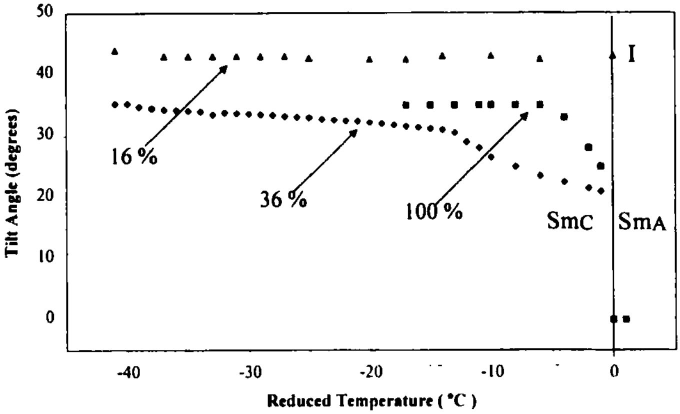

FIGURE 4. The temperature dependence of the tilt angle in the pure siloxane nitrostilbene (100%), and in mixtures with Br11-Si$_3$ containing 16% and 36% by weight of the siloxane nitrostilbene dye.

the conformation of the host; the only mesophase displayed is a SmC* phase with a temperature independent tilt of 43 degrees identical, within experimental errors, to that of the host (44 degrees). At 36% w/w concentration the dye imposes its conformation and characteristics on the material. There is a SmA* phase and a SmC* phase. On cooling, the tilt angle varies rapidly close to the SmA* / SmC* transition and then is almost temperature independent, it varies from 30 degrees to 34 degrees over 30°C temperature range. The tilt angle is very close to that observed in the pure organosiloxane dye (35 degrees). A systematic study of the behaviour of the tilt angle in mixtures with concentration of dye between 36% w/w and 16% w/w is currently in progress.

Dye % w/w	Phase Sequence	Tilt deg	Ps nC/cm^2	Resp μs
100	$I \xleftrightarrow{105} Sm_A \xleftrightarrow{55} Sm_C \xleftrightarrow{37} K$	35	-	-
36	$I \xleftrightarrow{108} Sm_A^* \xleftrightarrow{68} Sm_C^* \xleftrightarrow{<20} K$	34	<5	500
16	$I \xleftrightarrow{95} Sm_C^* \xleftrightarrow{20} K$	43	70	400
0	$I \xleftrightarrow{88} Sm_C^* \xleftrightarrow{46} K$	44	87	300

TABLE 1. The characteristics of the mixtures between siloxane-nitrostilbene and Br11-Si_3. The concentrations are the weight percentage of the dye in the mixture, the transition temperatures, determined by optical microscopy, are in degrees Celsius; the tilt angle, spontaneous polarisation and response time to a step voltage (~10 V/μm) were measured at the reduced temperature of $-10\ ^0C$; the time quoted here is the delay between the voltage step and the current peak due to the reversal of the polarisation.

Mixtures with Br11-Si3-11Br

The dye is also miscible at all concentrations in the antiferroelectric bi-mesogen Br11-Si_3-11Br material. The characteristics of some selected mixtures are summarised in table 2. All the mixtures characterised are antiferroelectric; this is in agreement with the model described in reference [9] which implies that a small percentage of V-shaped organosiloxane molecules such as Br11-Si$_3$-11Br in a monomeric organosiloxane material imposes an anticlinic arrangement of the molecules on the material. The V-shape has been confirmed by dynamic polarised Raman spectroscopy[14].

Dye % w/w	Phase Sequence	Tilt deg	Ps nC/cm^2	Resp μs
100	$I \xleftrightarrow{105} SmA \xleftrightarrow{55} SmC \xleftrightarrow{37} K$	35	-	-
50	$I \xleftrightarrow{148} SmA^* \xleftrightarrow{95} SmC^*_A \xleftrightarrow{<20} K$	35	<5	400
36	$I \xleftrightarrow{138} SmA^* \xleftrightarrow{112} SmC^*_A \xleftrightarrow{<20} K$	22.5	16	250
0	$I \xleftrightarrow{106} SmC^*_A \xleftrightarrow{50} K$	43.5	135	300

TABLE 2. The characteristics of the mixtures between Br11-Si$_3$-11Br and the siloxane-nitrostilbene. See legend of table 1 for the experimental details.

Other Mixtures

We have prepared mixtures where the number of silicon atoms in the host is different from that in the guest molecule. The dye appears to be continuously miscible in Cl11-Si$_4$-11Cl. The mixture containing 42% w/w of dye displays a SmC* phase at room temperature, a transition to a SmA* phase at 100°C and clears at 141°C. In the ferroelectric phase, under the same experimental conditions as in table 1, the response time is 200μs and the temperature independent tilt angle is 22.5 degrees, the ideal angle for some birefringent display devices applications

If the numbers of silicon atoms in the host and the guest are too dissimilar, the materials may segregate. For example a mixture containing 45% w/w of the siloxane dye (with three silicon atoms) in F11-Si$_7$-11F (with seven silicon atoms) is biphasic at all temperatures in the mesomorphic range.

CONCLUSIONS

The test material presented in this paper confirms that the *effective* or *virtual backbone effect* in low molar mass organosiloxane liquid crystals can be used to increase (up to 100% in some cases) the solubility of a dye guest moiety in a liquid-crystalline host. The grafting of the siloxane group on the guest moiety does not affect, in most cases, the functionality of the guest and may induce mesomorphic phases in some non-mesogenic guests. The ferroelectric / antiferroelectric characteristics of the liquid-crystal host can be retained or advantageously controlled by the guest. This opens a new avenue for the design of dichroic, fluorescent or light-emitting materials with response times in the microsecond range. The principle could also be extended to paramagnetic moieties[15] to prepare organosiloxane magnetic liquid-crystal materials suitable for applications.

Acknowledgements
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References

[1] H.J. Coles, I. Butler, K. Raina, J. Newton, J. Hannington and D. Thomas, *SPIE* **2408,** 14–21. (1995)

[2] H.J. Coles, H. Owen, J. Newton and P. Hodge, *SPIE* **2408,** 22–29. (1995)

[3] H.J. Coles, H. Owen, J. Newton and P. Hodge, *Liquid Crystals,* **15,** 739–744 (1993)

[4] J. Newton, H.J. Coles, P. Hodge and J. Hannington *J. Mater. Chem.* **4,** 869 (1994)

[5] J. Naciri, J. Ruth, G. Crawford, R. Shashidar and B.R. Ratna, *Chem. Mat.* **7,** 1397, (1995)

[6] H. Owen, H.J. Coles, J. Newton and P. Hodge, *Mol., Cryst. and Liq. Cryst.,* **257,** 151–159, (1994)

[7] J. Newton, H.G. Walton, H.J. Coles, and P. Hodge, *Mol., Cryst. and Liq. Cryst.,* **260,** 107–125, (1995)

[8] M.J. Coles, C. Carboni, H.J. Coles, *Ferroelectrics,* **212,** 179–186, (1998)

[9] C. Carboni and H.J. Coles, Proc 17th ILCS, Strasbourg (1998)

[10] P.J. Sebastiano, S.Mery, M. Sieffert, J.F. Nicoud, Y. Galerne and D. Guillon, *Ferroelectrics,* **212,** 33–141 (1998)

[11] W.K. Robinson, P. Kloess, C. Carboni and H.J. Coles *Liq. Cryst.,* **23,** 309–312 (1997)

[12] C. Carboni, W.K. Robinson, S. Perkins and H.J. Coles, *Ferroelectrics,* **212,** 161–168, (1998)

[13] W.K. Robinson, P. Kloess, C. Carboni and H.J. Coles, *Liq. Cryst.,* **25,** 301–307 (1998)

[14] S. Meyer and H.J. Coles, *In preparation*

[15] I.M. Saez, G.H. Mehl, E. Sinn and P. Styring, *Journal of Organometallic Chemistry,* **551,** 299 (1998)