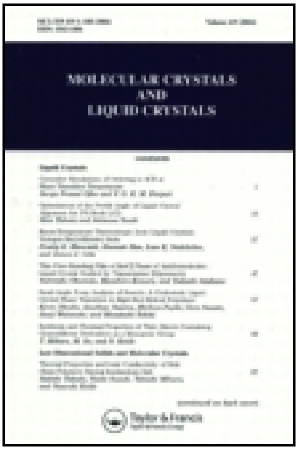


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Bi-Mesogenic Fluorinated Organosiloxanes: an Electro-Optic Study Revealing Unusual Phase Behaviour

W. K. Robinson [a] , P. Lehmann [a] & H. J. Coles [a]

[a] Department of Physics and Astronomy, Southampton Liquid Crystal Institute, University of Southampton, Southampton, SO17 1BJ, UK

Version of record first published: 24 Sep 2006

To cite this article: W. K. Robinson, P. Lehmann & H. J. Coles (1999): Bi-Mesogenic Fluorinated Organosiloxanes: an Electro-Optic Study Revealing Unusual Phase Behaviour, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 328:1, 229-236

To link to this article: http://dx.doi.org/10.1080/10587259908026063

Mol. Cryst. Liq. Cryst., 1999, Vol. 328, pp. 229-236
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Bi-Mesogenic Fluorinated Organosiloxanes: an Electro-Optic Study Revealing Unusual Phase Behaviour

W. K. ROBINSON, P. LEHMANN and H. J. COLES*

Department of Physics and Astronomy, Southampton Liquid Crystal Institute, University of Southampton, Southampton, SO17 1BJ, UK.

The physical characteristics of a new fluorinated organosiloxane material are presented, and compared to those of its non-fluorinated homologue. The fluorinated material has a high Ps (200 – 450 nC/cm^2) and a high tilt angle (~38°) over a 100°C wide temperature range. Both materials exhibit antiferroelectric phases. As the fluorinated material is cooled, its behaviour becomes more ferroelectric-like. We discuss this behaviour in relation to the molecular structure of the materials.

Keywords: organosiloxanes; antiferroelectricity; fluorine

INTRODUCTION

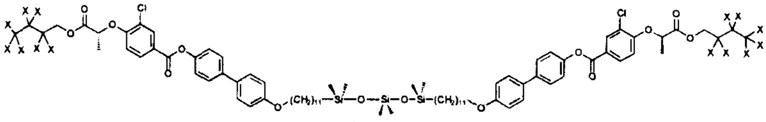
Organosiloxanes have been the subject of much investigation because of their ability to combine the fast switching times of low molecular mass (LMM) materials with the ruggedness of polymers.[1] The enhanced mechanical stability of organosiloxanes is believed to derive from the microphase separation of the siloxanes and the aromatic parts of the molecule to form separate sub-layers. Recently we have reported the appearance of antiferroelectricity in a new series of LMM organosiloxane materials.[2] We have concluded that the driving force behind the antiferroelectric behaviour of these materials is the conformal shape of the siloxane spacer. In this paper we study an organosiloxane molecule with perfluorinated end chains. Fluorocarbons are known to be highly incompatible with both saturated and aromatic hydrocarbons.[3] They may therefore form an extra sub-layer in organosiloxane materials, leading to modified phase behaviour.

---

* Author for correspondence.

EXPERIMENTAL

The structural formulae of the materials studied, denoted Si3(X)3, where X = either F or H, is shown below. Details of the synthesis, phase characterisation, and structure property correlations can be found elsewhere.[4]



Si3(X)3

Si3(F)3:	Heating: **Cr1** 35 **Cr2** 71 **Cr3** 80 **SmI*** 101 **SmC**$^*_A$ 131 **I** Cooling: **I** 130 **SmC**$^*_A$ 96 **SmF*** 32 **Cr1**
Si3(H)3:	**I** 77 **SmC**$^*_A$ 35 **SmB**

TABLE 1 Phase transition temperatures (in °C) of materials studied.

The effect of perfluorination

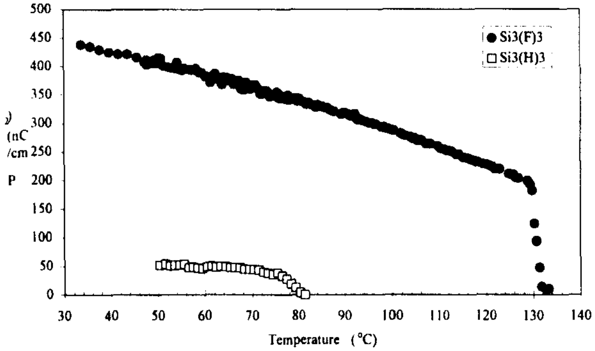


FIGURE 1 The temperature dependence of the induced polarisation, P.

The phase range of Si3(F)3 is extended compared to that of Si3(H)3, but the melting point is increased and the material shows a tendency to form monotropic phases. Figure 1 shows the induced polarisation, measured by the current pulse technique, as a function of temperature for Si3(F)3 and Si3(H)3. Both materials show antiferroelectric phases as expected.[2] The threshold voltages required to switch Si3(H)3 are much higher than those required to switch Si3(F)3, and Si3(H)3 also takes longer to relax back into its antiferroelectric state. (e.g. at (T_C-10)°C Si3(H)3 switches at -13.3 V/μm, and relaxes at 3.1 V/μm, whereas Si3(F)3 switches at –2V/μm and relaxes at 7V/μm under a quasi-static field.) The sign of the polarisation was found to be positive in both materials. The polarisation was found to increase monotonically as the temperature was reduced from Tc, with a discontinuity at T_C which is typical for first order phase transitions such as I-SC^*_A.

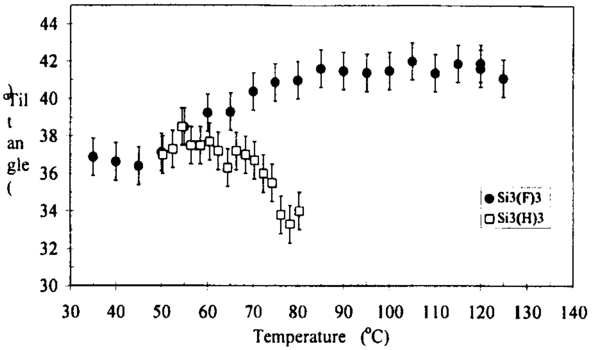


FIGURE 2 Temperature dependence of the tilt angle

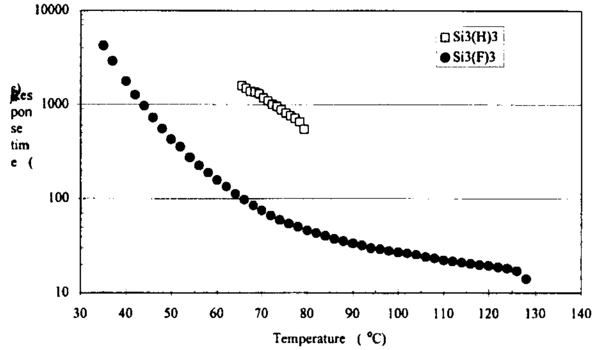


FIGURE 3 Temperature dependence of the response time.

The temperature dependence of the tilt angle is shown in figure 2. The tilt angles are observed to be high (37-41°). Again both materials exhibit a jump in the tilt angle at T_C typical of a first order transition. The tilt angle of Si3(H)3 then increases smoothly with decreasing temperature until saturation is reached. Si3(F)3 shows a decrease of tilt angle, beginning at ~90°C, after an initial temperature independence. This decrease occurs shortly after the observed phase change at 96°C. The tilt angle flattens off again at ~50°C.

Figure 3 shows the temperature dependence of the response time from field reversal until 50% of the sample is switched by a driving field of 12V/μm. Switching times for the perfluorinated material are much faster than those for the non-fluorinated compound, as might be expected due to its

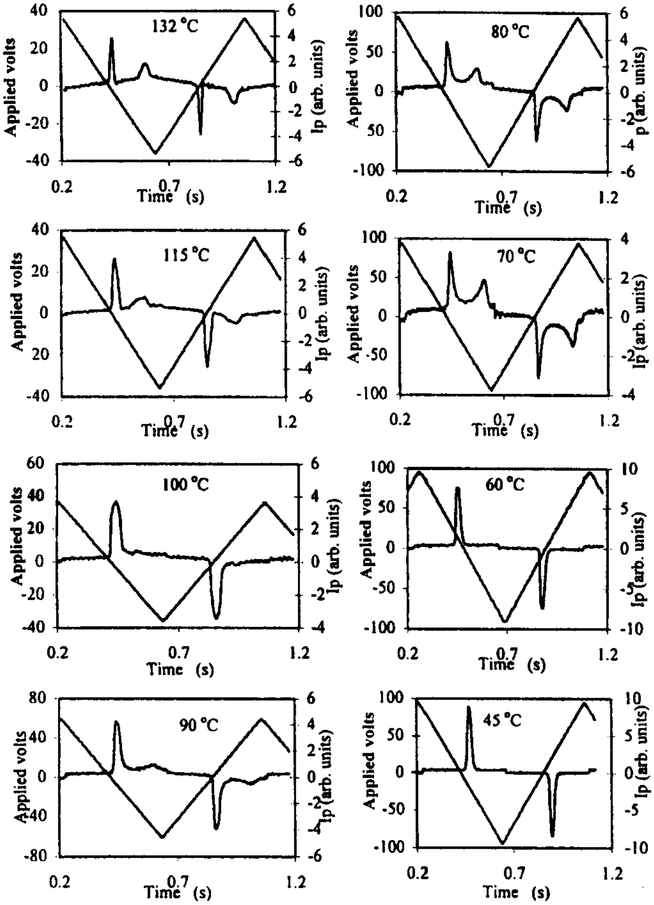


FIGURE 4 Current pulse (Ip) responses and applied voltage at various temperatures for Si3(F)3. Note the increase in applied voltage at 90°C and again at 80°C.

higher polarisation. Si3(H)3 shows Arrhenius type behaviour, with an activation energy of 0.74 eV. Si3(F)3 does not show Arrhenius type behaviour, but this may be expected for a material that possesses more than one ferroelectric or antiferroelectric mesophase.

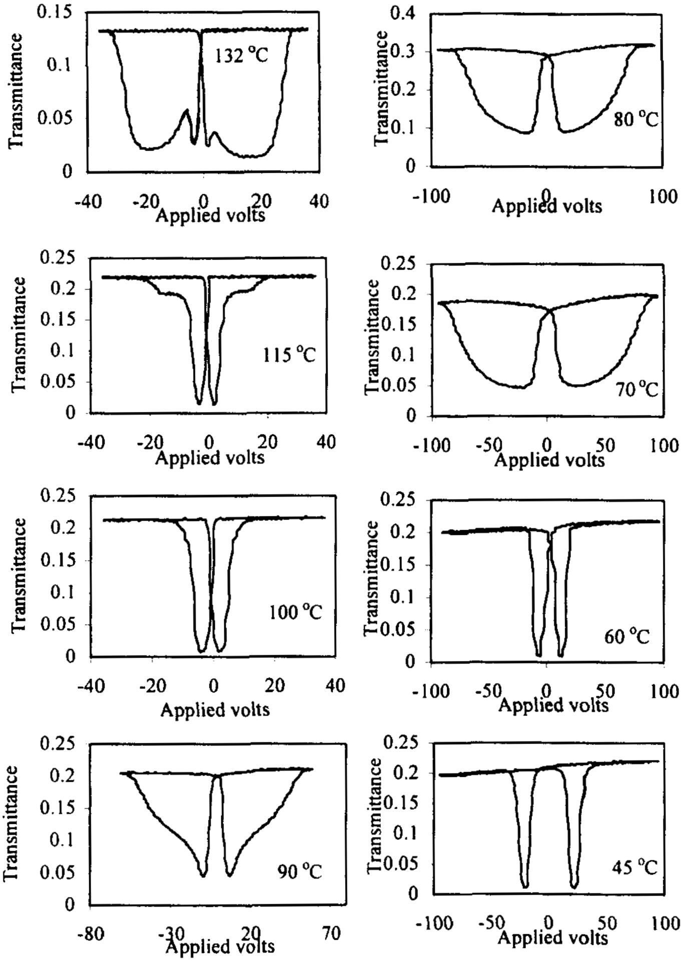


FIGURE 5 Optical hysteresis loops at various temperatures for Si 3(F)3. Note the increase in applied voltage for loops at 90°C and again at 80°C.

Switching behaviour of Si3(F)3

A study of the switching behaviour was carried out in order to elucidate whether the material exhibited ferroelectric or antiferroelectric properties. Switching current traces as a function of time, and optical transmittance loops and can be seen in figures 4 and 5. All data were recorded using a 1.2 Hz triangular wave. It can be seen that the material displays a characteristic antiferroelectric response (double current pulse and three different optical states) immediately after the transition from the isotropic phase. As the material is cooled the response becomes progressively less antiferroelectric-like. The material is still antiferroelectric at temperatures down to 96°C. Below 96°C the behaviour of the material changes, and again two prominent peaks are displayed which are coincident with the changes between the three different optical states observed. At ~60°C the switching changes again, giving a typical ferroelectric response, as evinced by a single current peak and only two optical switching states. This behaviour persists regardless of how slowly the material is switched.

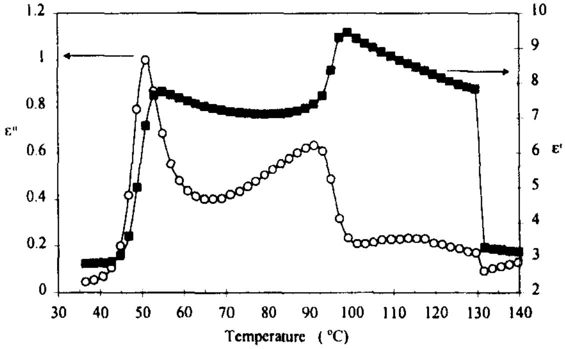


FIGURE 6 Temperature dependence of the real (ε') and imaginary (ε") parts of the permittivity for Si3(F)3 measured on cooling at a frequency of 1000 Hz.

Dielectric properties

The permittivity measurements were performed with Si3(F)3 over a frequency range of 20 – 3×10^5 Hz. The temperature dependence of the real (ε') and imaginary (ε") parts of the permittivity measured on cooling are shown in figure 6. Both curves exhibit anomalies at ~95°C and ~60°C. From the frequency dispersions detected at various temperatures we calculated relaxation frequencies, f_r, for processes contributing to the permittivity. The temperature dependence for f_r is shown in figure 7 and confirms the features shown in Figure 3 for the response times of Si3(F)3.

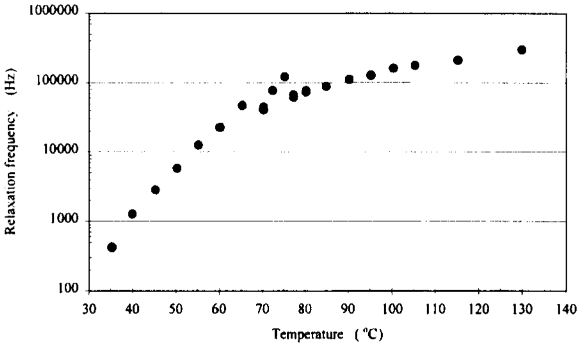


FIGURE 7 Temperature dependence of relaxation frequency of Si 3(F)3.

DISCUSSION

Perfluorinated chains are more ordered than their hydrocarbon homologues and are consequently much stiffer and bulkier. Hence fluorinated chains diminish the packing differences between the cores and the tails, and can introduce additional steric hindrance to the optimal packing of molecules.

The effect of perfluorination on the organosiloxane molecule studied has been to lower threshold voltages, to increase switching speed, to increase phase transition temperatures and to enhance the appearance of hexatic phases. We have observed that Si3(F)3 may exhibit three mesophases (see figs. 4 - 7). The nature of the lower temperature phases has not yet been established beyond doubt. Texture studies have indicated that the phase below 96°C is likely to be the SF* phase.[4] There are two possible explanations for the tristable switching observed from 96 – 60°C. Either the phase is helicoidal ferroelectric, or it is antiferroelectric. Helical ferroelectric and antiferroelectric structures can produce the same qualitative time dependencies in current pulse and optical responses, due to the helix unwinding and reforming.[5] In this case, the phase transition at 60°C observed in the switching characteristics (see figures 4 and 5) is a result of the increased pitch length making this effect unobservable. The decrease in strength of antiferroelectricity in the high temperature phase (130 – ~96°C) is expected if the sample becomes ferroelectric.

The possibility that the phase observed between 96 and 60°C may be antiferroelectric cannot be ruled out. In this case the phase becomes ferroelectric on cooling. In the SC* case the antiferroelectric phase is more ordered than the ferroelectric and so it occurs at a lower temperature. However a ferroelectric SI phase has been observed to emerge as the lower temperature phase to SI$^*_A$.[6]

The question remains as to what drives a sample to become ferroelectric. It is thought that the ferroelectric SC* phase is stabilised by packing entropy resulting from the excluded volume effect.[7] However, we have observed that the tilt angle decreases in this material. Equally, the forces that produce the antiferroelectricity in our material may be decreasing with decreasing temperature. Antiferroelectricity in LMM materials is believed to be caused by the pairing of transverse molecular dipole moments in adjacent smectic layers.[8] In our case we believe that the antiferroelectricity is caused by a conformal effect of the siloxane chain.[4,9] The changing dielectric nature of the material implies that the conformal effect causing the antiferroelectricity is not the main driving force behind the molecular organisation at lower temperatures.

We intend to investigate the temperature dependence of the pitch of this material, and carry out X-ray studies in order to determine the nature of the phase below 96°C. Preliminary data indicates there is no significant change in layer spacing on cooling.[10]

Acknowledgements. HJC thanks the EPSRC for support for this programme under grant GR/K/70908.

References

[1] H.J. Coles, H. Owen, J. Newton and P. Hodge, *Liquid Crystals,* **15** 739 (1993). H. Poths, R. Zentel, *Liquid Crystals,* **16** 749 (1994).

[2] W.K. Robinson, P.S. Kloess, C. Carboni and H.J. Coles, *Liquid Crystals,* **23** 309 (1997).

[3] J.H. Hildebrand and R.L. Scott, *Regular Solutions,* Prentice Hall, (1962).

[4] P. Lehmann, W.K. Robinson, and H.J. Coles, Proceedings 17th ILCC, Strasbourg (1998).

[5] M. Glogarova, L. Lejcek, J. Pavel, U. Janovec and J. Fousek, *Czech. J. Phys.,* **B32** 943 (1982).

[6] M. Neundorf, Y. Takanishi, A. Fukuda, S. Saito, K. Murashiro, T. Inukai and D. Demus, *J. Mater. Chem.,* **5** 2221 (1995).

[7] M. Nakagawa, *J. Phys. Soc. Jpn.,* **62** 2260 (1993).

[8] Y. Takanishi, K. Hiraoka, V.K. Agrawal, H. Takezoe, A. Fukuda, and M. Matsushita, *Jpn. J. Appl. Phys.,* **30** 2023 (1991).

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

[10] D. Guillon, Private Communication.