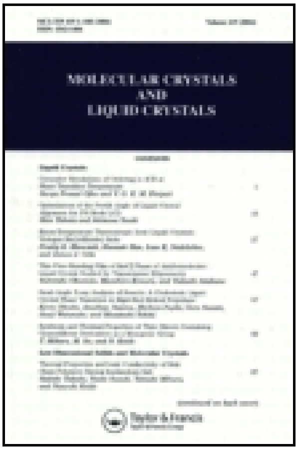

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Novel Room Temperature Fluorinated Ferroelectric Organosiloxane Liquid Crystal Mixtures

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Novel Room Temperature Fluorinated Ferroelectric Organosiloxane Liquid Crystal Mixtures

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In this paper we present the results of mixing fluorinated and non-fluorinated organosiloxane materials based on ferroelectric and antiferroelectric low molar mass organosiloxane (LMMO) liquid crystals. None of the fluorinated materials exhibit a mesophase, however when mixed with the non-fluorinated analogues a ferroelectric phase is observed. We present the resultant phase diagrams together with the spontaneous polarisation curves of the mixtures.

Keywords: Ferroelectric; Antiferroelectric; Organosiloxane; Fluorine; Room Temperature

INTRODUCTION

Low molar mass organosiloxane (LMMO) liquid crystals, as shown in figure 1, display both ferroelectric and antiferroelectric behaviour [1] depending only on the nature of the siloxane moiety. The monomeric (AB) materials display only ferroelectric behaviour with spontaneous polarisations of between 50 and 100 nC/cm^2, and tilt angles that are close to 45° and independent of temperature. However, the dimeric (ABA) materials exhibit either ferroelectric or antiferroelectric behaviour dependant upon the lateral halogen substituent and the number of silicon atoms in the siloxane spacer. For materials with 3

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units in the siloxane chain the phase behaviour is purely antiferroelectric regardless of the nature of the halogen substituent. Again the P_s is of the order of $100 nC/cm^2$ and the tilt angle is close to 45° and independent of temperature. The antiferroelectricity is attributed to the siloxane moiety conferring a bent conformation on the molecule rather than antiferroelectric interactions between the layers [1].

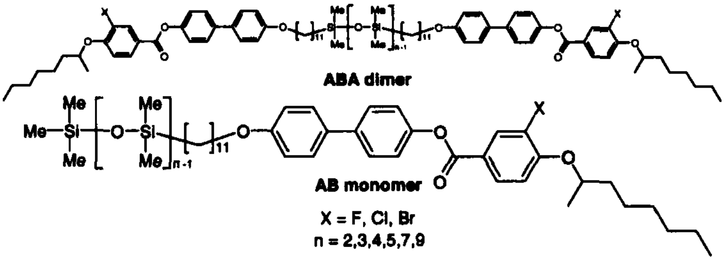
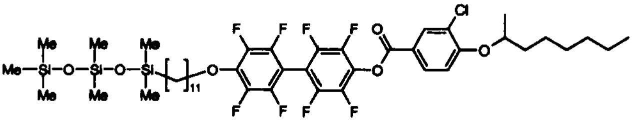


FIGURE 1 Structure of the organosiloxane mesogens.

These materials possess some of the robust mechanical properties of polymers, perfect bistability and the fast electro-optic response of low molar mass liquid crystals and therefore make ideal candidates for use in ferroelectric or antiferroelectric display devices. However, the transition temperatures are not ideal with all transitions being above room temperature [1]. It is well known that lateral fluorination in the aromatic core of liquid crystals can dramatically reduce transition temperatures [2,3]. We have reported previously on the properties of mixtures of the fluorinated material shown in figure 2 and the non-fluorinated analogue [4]. The two components were found to be completely miscible, as shown in figure 3, together with the spontaneous polarisation curves for the various mixtures. This was despite the incompatabilities expected between the fluorinated and non-fluorinated moieties. We attribute this to the siloxane moieties aggregating and thus aiding the miscibility of unlike mesogenic materials. This approach has been used to great effect in dye guest host devices where the solubility of a siloxane containing dye molecule is greatly increased in these LMMO liquid crystal hosts [5,6,7]. However, it can be seen in figure 3 that, despite the miscibility, $Cl_{11}(F_8)\text{-}Si_3$ has too low a melting point to be useful in these mixtures. Therefore we have prepared analogous materials, with a reduced amount fluorination, as shown in figure 4, in an attempt to produce better mixtures.



$Cl_{11}(F_8)$-Si_3

FIGURE 2 Structure of the fully fluorinated organosiloxane.

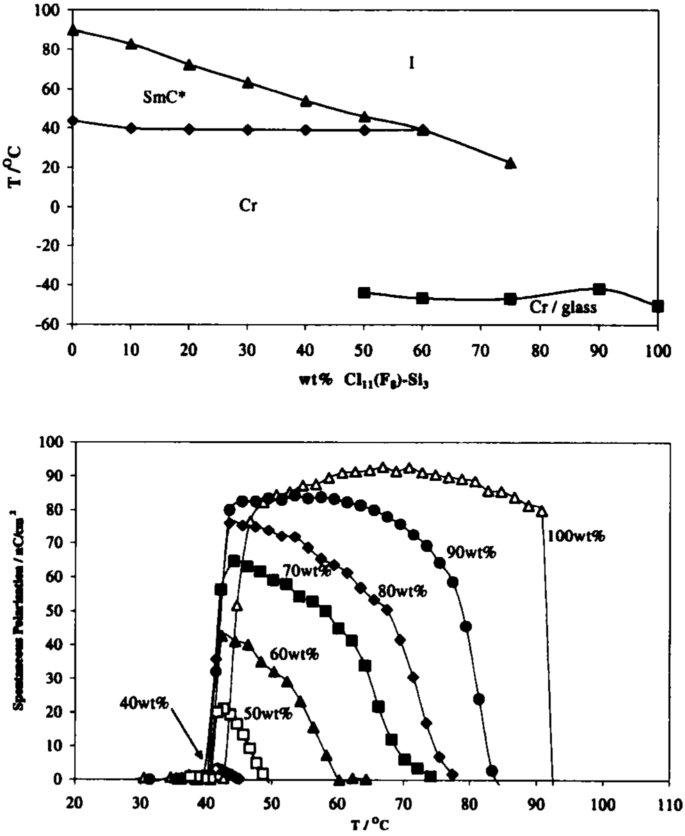
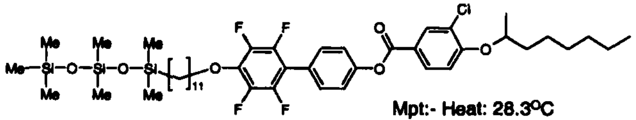
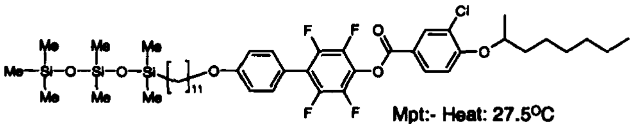


FIGURE 3 The phase diagram (top) and spontaneous polarisation curves (bottom) for mixtures of $Cl_{11}(F_8)$-Si_3 and Cl_{11}-Si_3.



$Cl_{11}(F_4ether)$-Si_3

Mpt:- Heat: 28.3°C
Cool: 11.5°C



$Cl_{11}(F_4ester)$-Si_3

Mpt:- Heat: 27.5°C
Cool: 1.6°C

FIGURE 4 Structure of the partially fluorinated organosiloxanes.

SYNTHESIS

The full synthetic details can be found in the following references [4,8,9].

CHARACTERISATION

All the mixtures were characterised using a combination of optical microscopy and differential scanning calorimetry. The spontaneous polarisations (P_s) were determined using the current pulse technique [10], using 3.2μm cells with anti-parallel rubbed polyimide alignment.

RESULTS

Figure 5 shows the phase diagram obtained on cooling various mixtures of Cl_{11}-Si_3 and $Cl_{11}(F_4ester)$-Si_3. As can be seen, the fluorinated material is completely miscible in the non-fluorinated host, with the SmC* – I transition temperature steadily decreasing as the amount of $Cl_{11}(F_4ester)$-Si_3 is increased until, for the pure fluorinated material, the mesophase is completely extinguished. Unlike the and $Cl_{11}(F_8)$-Si_3 /Cl_{11}-Si_3 mixtures the melting point does not remain constant, with some of the mixtures cooling into a glassy phase.

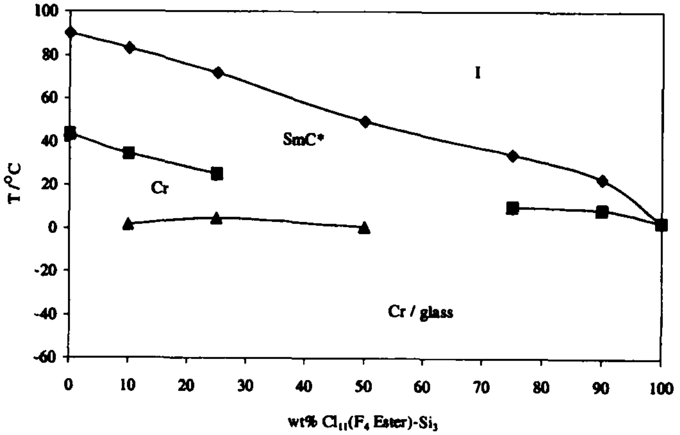


FIGURE 5 Phase diagram observed for a mixture of $Cl_{11}(F_4ester)$-Si_3 and Cl_{11}-Si_3.

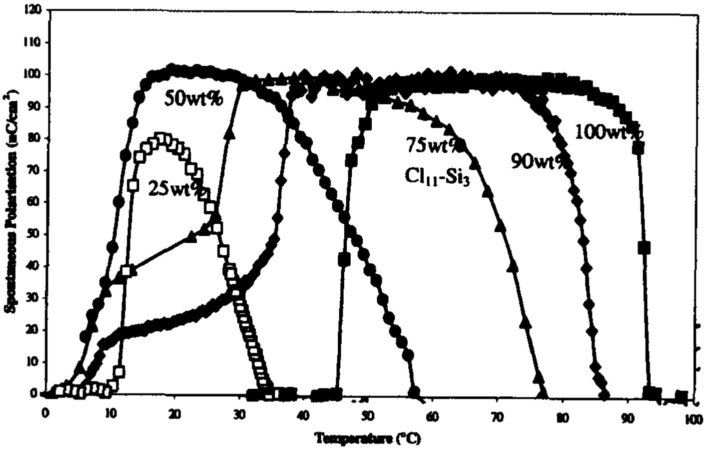


FIGURE 6 Spontaneous polarisations for different mixtures of $Cl_{11}(F_4ester)$-Si_3 and Cl_{11}-Si_3.

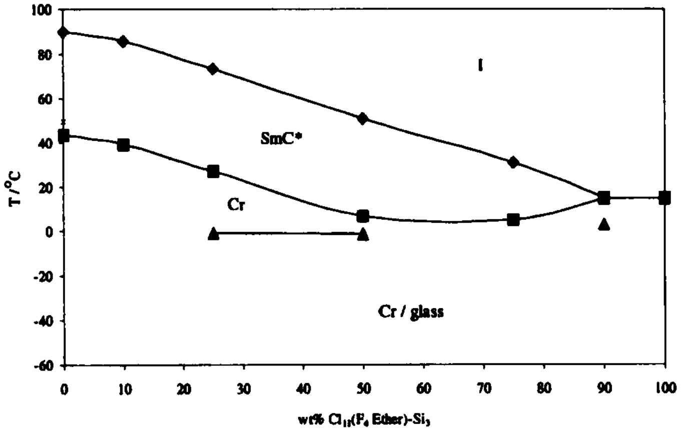


FIGURE 7 Phase diagram observed for a mixture of $Cl_{11}(F_4ether)$-Si_3 and Cl_{11}-Si_3.

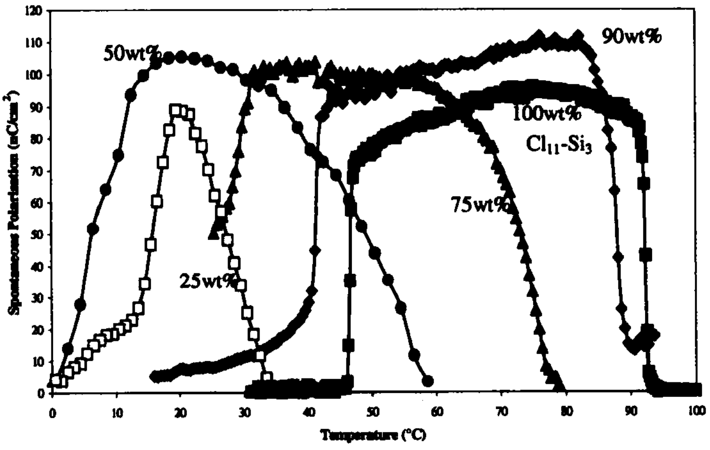


FIGURE 8 Spontaneous polarisations for different mixtures of $Cl_{11}(F_4ether)$-Si_3 and Cl_{11}-Si_3.

Figure 6 shows the spontaneous polarisation curves obtained for the different mixtures of Cl_{11}-Si_3 and $Cl_{11}(F_4$ether)-Si_3. Unlike that seen for the fully fluorinated $Cl_{11}(F_8)$-Si_3 mixtures, the P_s does not decrease as the concentration of fluorinated material increases. In fact the P_s remains at an almost constant 100nC/cm^2 for mixtures containing up to 50wt% $Cl_{11}(F_4$ester)-Si_3, however this begins to fall at higher concentrations.

Figure 7 shows the phase diagram obtained on cooling various mixtures of Cl_{11}-Si_3 and $Cl_{11}(F_4$ether)-Si_3. Again it can be seen that both components are completely miscible and there is a steady decrease in the SmC* – I transition temperature until, for 100wt% $Cl_{11}(F_4$ether)-Si_3, the mesophase vanishes.

Figure 8 shows the spontaneous polarisation curves obtained for the different mixtures of Cl_{11}-Si_3 and $Cl_{11}(F_4$ether)-Si_3. Not surprisingly the behaviour is very similar to that seen for $Cl_{11}(F_4$ester)-Si_3, with the P_s remaining almost constant at ~100nC/cm^2 for concentrations up to 50wt% $Cl_{11}(F_4$ether)-Si_3, at which point they begin to decrease.

CONCLUSIONS

We have prepared a number of novel fluorinated organosiloxane materials containing either 4 or 8 fluorine atoms. Although none of the fluorinated materials exhibit liquid crystalline phases, ferroelectric phases are observed when these materials are mixed with the non-fluorinated analogues. The phase diagrams show that for all of the fluorinated materials there is a steady decrease in the SmC* – I phase transition upon decreasing the concentration of Cl_{11}-Si_3, with the mesophase being observed over the whole concentration range for those materials containing only 4 fluorine atoms. The spontaneous polarisation for mixtures containing $Cl_{11}(F_8)$-Si_3 scale essentially linearly as the concentration of Cl_{11}-Si_3 is reduced, whereas they remain almost constant for both $Cl_{11}(F_4$ ester)-Si_3 and $Cl_{11}(F_4$ ether)-Si_3 as the concentration of Cl_{11}-Si_3 is reduced. For mixtures containing greater than 50wt% Cl_{11}-Si_3 a P_s of the order of 100nC/cm^2 are observed for both $Cl_{11}(F_4$ ester)-Si_3 and $Cl_{11}(F_4$ ether)-Si_3. This behaviour results in mixtures possessing room temperature ferroelectric phases with high spontaneous polarisations.

ACKNOWLEDGEMENTS

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