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New low molar mass organosiloxanes with unusual ferroelectric properties

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A new low molar mass chiral organosiloxane mesogen and its racemic analogue have been synthesized and their mesomorphic and ferroelectric properties investigated. The chiral derivative, denoted A*B, exhibits one tilted enantiotropic ferroelectric smectic C mesophase over a broad temperature range, with very high tilt angles and moderate spontaneous polarization (36° and 19 nC cm^{-2} at 20°C). The achiral siloxane derivative, denoted A$^{(\pm)}$B, exhibits one broad enantiotropic smectic C phase. Preliminary electro-optic measurements indicate that the spontaneous polarization is weakly dependent on temperature between 10°C and 50°C, the latter being the S_C^* to isotropic phase transition. The tilt angle and layer spacing are temperature independent, and current response times of less than 200 μs were measured at 25°C for fields of 10 V μm^{-1}. These results are discussed in comparison with those for side chain polymer liquid crystal structures and other low molar mass ferroelectric materials.

Low molar mass (LMM) liquid crystalline materials exhibiting chiral smectic C (S_C^*) phases have been studied extensively because of their ferroelectric properties [1, 2] their fast response times ($\sim\mu$s) in pulsed DC electric fields [3], and their great potential for complex displays [4]. More recently, side-chain liquid crystal polymers (SCLCP), in which pendant mesogenic and chiral side groups have been attached via a spacer group to a flexible or semi-flexible polymer backbone, have been synthesized [5–7] and shown to exhibit S_C^* phases. The presence of the polymer backbone leads, in general, to a broader mesophase range, suppression or reduction of the tendency to form crystalline phases, by inducing glassy phases, and an increase in the mesophase clearing temperature [8] in comparison with the equivalent LMM mesogenic side group moiety. Polysiloxanes in general have much lower glass transition temperatures, T_g, than their more rigid polyacrylate or methacrylate counterparts. Whilst the presence of the polymer backbone broadens the phase stability and improves the mechanical properties, it is the side group mesogen that confers the specific electro-optic or ferroelectric properties on the SCLCP. In recent studies, [9–11] ferroelectric switching on the millisecond time-scale was observed for a variety of SCLCP systems and a mechanically flexible display was demonstrated [11]. These results illustrate the potential for the fabrication of rugged displays. The ruggedness is due, presumably, to the stabilization of the layer structure by the polymer backbone. The results also indicate that the response times of the polymers, in the S_C^* phase, are orders of

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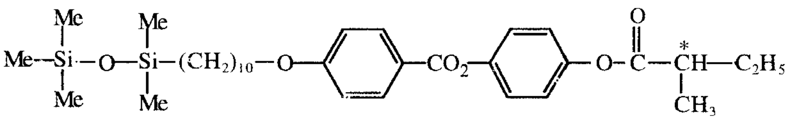
magnitude slower than their LMM counterparts under similar applied fields and reduced temperatures. These significantly longer response times must be related to the increased viscosity of the polymer systems, which following the Mark–Houwink equation, might be expected to scale [12] as a power law of the molecular weight, M_w. In contrast, however, a reduction in the glass transition temperature should help to decrease the viscosity, at a given reduced temperature, and thereby produce faster electro-optic response times [13]. Hence there is a growing interest in polysiloxane-based materials with their inherently low glass temperatures. The contrasting requirements of ruggedness (by incorporation of high M_w polymer structures) and low viscosity (by reduction of M_w and T_g) appear to limit the range of application of these potentially fascinating materials.

As a compromise between the above advantages and disadvantages of the SCLCP systems, we have recently synthesized and studied a number of LMM organosiloxane mesogenic compounds [14, 15]. Materials have been prepared of the AB and ABA types where A refers to the mesogenic unit and B refers to a dimethylsiloxane chain or end chain spacer. For example, recently [16], using a modified form of the hydrosilylation route, we have synthesized a homologous series of mesogenic compounds based on the 4-(ω-alkenyoxy)-4′-cyanobiphenyl unit (A) and the pentamethyldisiloxane tail (B). Although the bulky, highly flexible disiloxane tail caused a reduction in the interchain interactions and the degree of crystallinity of the cyanobiphenyl precursor, it did not destroy the liquid crystallinity of these AB materials: quite the reverse was true and highly ordered broad temperature range smectic A rather than nematic phases were observed and confirmed by optical microscopy, X-ray scattering [17] and differential scanning calorimetry (DSC). This may be explained in terms of a ‘pseudo’ backbone within the phase due to the strong agglomeration of the siloxane units—the siloxane tails will tend to associate into a lower energy arrangement in the presence of other siloxane units. In this way the siloxane units helped to induce a well-defined layer structure in these organosiloxane LMM compounds similar to that found in SCLCP systems.

The electro-optic properties of both AB and ABA compounds were surprising. Response times in the S_A phase were virtually independent of temperature, switching threshold voltages were reduced in comparison with similar alkyloxycyanobiphenyl compounds, and two frequency switching mechanisms were observed [15] with a lower threshold voltage for DC switching than for AC switching. Thus these LMM organosiloxane mesogens appear to have well-defined layer structures similar to SCLCPs, whilst maintaining the faster electro-optic response times of more conventional organic LMM mesogens. Based on these properties, we have extended the work to organosiloxane LMM materials forming S_C^* mesophases.

The purpose of the present paper is to present preliminary data on the ferroelectric properties of a new LMM organosiloxane exhibiting an S_C^* phase. The vinyl mesogen 4-[(*S*)-2-methylbutanoyloxy]phenyl 4-(9-decenyloxy)benzoate was prepared [18] in both its chiral (A*) and racemic forms ($A^{\pm}$), and then coupled by a hydrosilylation reaction with the hydropentamethyldisiloxane (B). This gave products with the following structure:



The phase types and sequences of the vinyl precursors and the chiral and achiral LMM organosiloxane compounds were confirmed by optical microscopy, DSC and X-ray scattering. These data, which will be reported in detail at a later date [18], confirm that the A*B chiral compound exhibits one enantiotropic S_C^* mesophase between 50·4°C and ~10°C whilst the racemate has an S_C phase beteeen 48·9°C and ~10°C. The endothermic peaks were narrow indicating a high degree of purity as also confirmed by NMR. At higher temperatures both compounds have isotropic phases, whilst at lower temperatures the phases are crystalline. The X-ray scattering patterns are in perfect agreement with the optical observations confirming the mesophase as smectic C*. They contain two sharp Bragg reflections in the small angle region in the ratio 1:2, corresponding to the smectic layering, and a diffuse band in the wide angle region (~4·6 Å) corresponding to the liquid-like conformation of the paraffinic chains and the disordered lateral arrangement of the aromatic cores in the smectic layers. The layer spacing of 35 Å was invariant with temperatures as was the tilt angle—see figure 1.

The electro-optic properties, tilt angle (θ_t), spontaneous polarization (P_s) and response times (τ) were measured in specially prepared 3 μm spacer cells with rubbed polyimide alignment layers deposited on ITO electrodes (5 mm × 5 mm). On cooling from the isotropic to the helielectric S_C^* phase, the neat A*B organosiloxane compound did not readily align on the rubbed polyimide layers. However, cooling the same material at 1°C min^{-1} in the presence of a 5 V μm^{-1} AC field at 100 Hz gave good planar uniform alignment. The aligned cell showed good optical switching in the presence of reversed polarity pulsed DC fields. The optical hysteresis curves indicated tilt angles greater than 22·5° when measured using an adapted electro-optic microscope. Using a specially constructed and semi-automated rig [19] the tilt angles were measured as a function of temperature for an applied continuous square wave field (E) of 10 V μm^{-1} at 0·1 Hz and a probing wave length of 632·8 nm. We confirmed that at each temperature and under these conditions the electro-optic switching was both saturated (with E) and ferroelectric in nature. As can be seen from figure 1, the tilt angle is virtually independent of temperature at a constant value of ~36°. This is presumably due to the first order nature of the phase transition from the isotropic to the helielectric

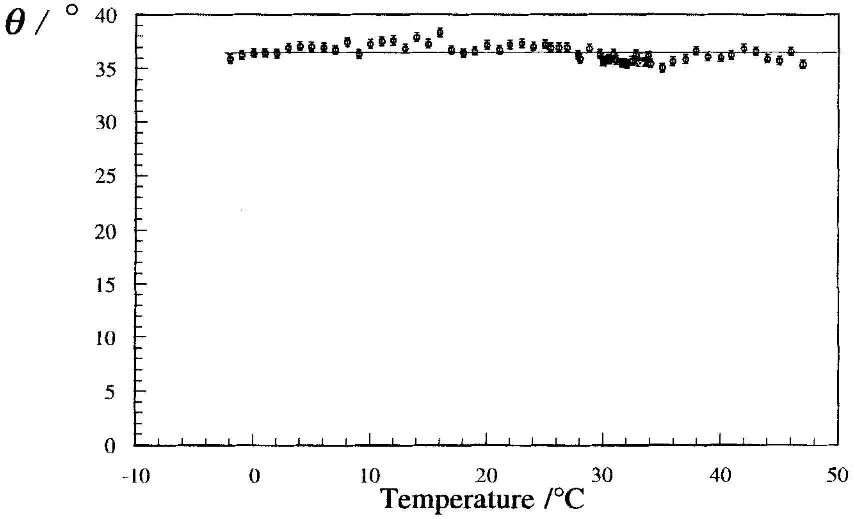


Figure 1. Dependence of projected optical tilt angle on temperature for $C_{10}A^*B$.

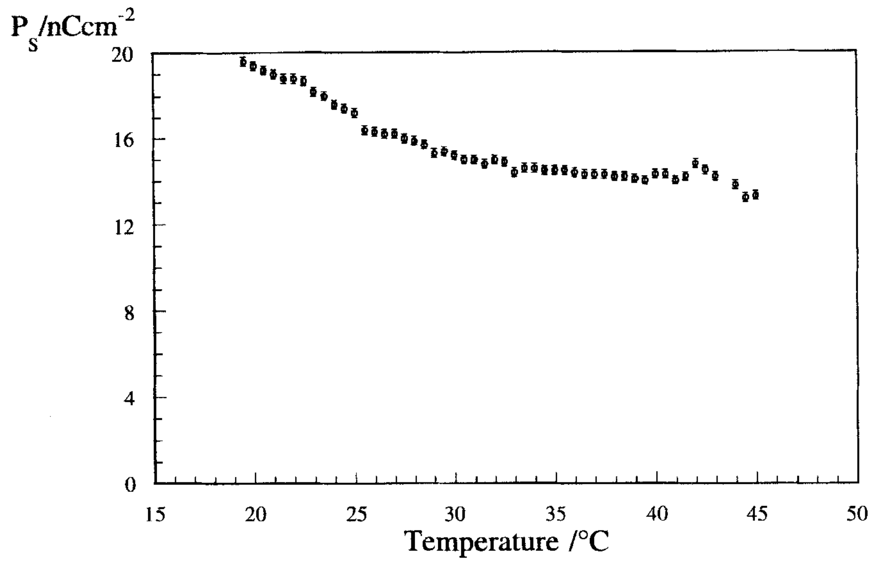


Figure 2. Dependence of spontaneous polarization on temperature for $C_{10}A^*B$.

phase at 50·4°C. It was possible to measure down to -2°C due to supercooling in the thin test cells. The spontaneous polarization was measured directly via the current pulse technique [20] using an applied triangular wave with a peak field of 10 V μm^{-1} at 70 Hz. This field again ensured saturation of the ferroelectric switching and the spontaneous polarization is given as a function of temperature in figure 2. As with θ_t the P_s is finite ($\sim$14 nC cm^{-2}) at the $I \rightarrow S_C^*$ transition due to the first order nature of this transition. Unlike θ_t, however the P_s increases slowly with decreasing temperature to reach 20 nC cm^{-2} some 32°C below the onset of the isotropic to S_C^* phase transition. This variation is, therefore, only of the order of a few nC cm^{-2} between 45°C and room temperature (25°C) and does not have the usual $(T^* - T)^{0 \cdot 5}$ behaviour. Since the tilt angles are greater than 22·5°, we did not measure response times in terms of the usual 10 per cent to 90 per cent change in maximum transmitted intensity for a sample placed between a crossed polarizer–analyser pair. For the present high tilt materials the data would have little meaning and we preferred to measure the current response time as that time taken from the field reversal to the peak of the current pulse when the sample was subject to a continuous square wave of 10 V μm^{-1} at 100 Hz. This response time is given as a function of temperature for different applied fields in figure 3. At 20°C the square wave response time, to 10 V μm^{-1}, was 210($\pm$10) μs. The commercially available and optimal SCE 13 S_C^* mixture (Merck Ltd, Poole, U.K.), under the same conditions, gave a current response time of 120($\pm$10) μs for a tilt angle of 22°. The P_s of the A*B and the commercial SCE 13 material are 19 nC cm^{-2} and 28 nC cm^{-2}, respectively. This difference in P_s is almost sufficient to explain the difference in the current response times (c.f., $\tau = \gamma / P_s E$, where γ is the projection viscosity). Since, however, the tilt angle of the organosiloxane (36°) is much greater than that for SCE 13 (22°), this suggests that the projection viscosity of the organosiloxane must be less than that for SCE 13. Using the current pulse technique, we measured the projection viscosity of the organosiloxane to be 0·5 Pa s and that of SCE 13 to be 0·85 Pa s at 20°C confirming this suggestion. Thus the neat organosiloxane is giving comparable response behaviour to that of current commercial mixtures and, with reduced tilt

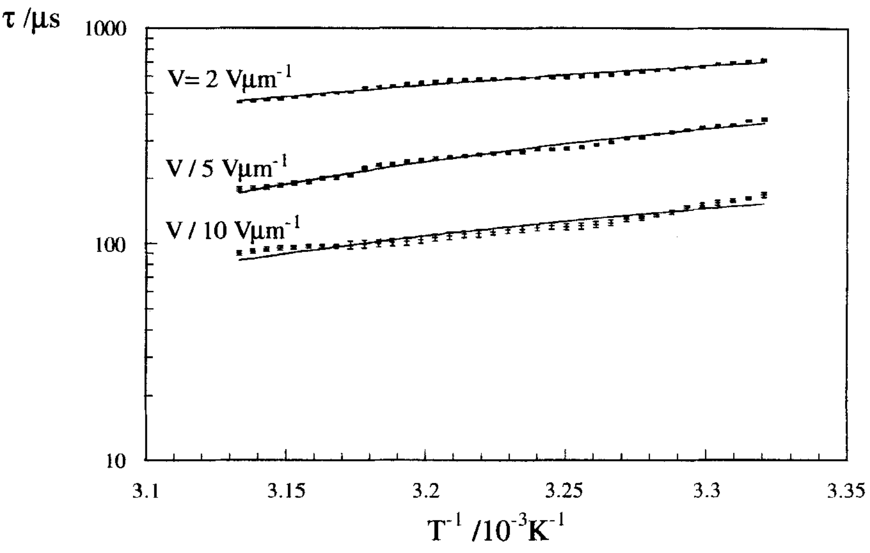


Figure 3. Dependence of current response times on temperature for $C_{10}A^{*}B$ at different applied electric field strengths (2, 5 and 10 V μm^{-1}).

angles and increased P_s, it should show further marked improvements. These ferroelectric response times are orders of magnitude faster than polymeric S_C^* materials switching under similar fields at room temperature [11]. Finally, on repeated cycling and switching in electric fields, no degradation was observed in the physical properties of these new LMM organosiloxane S_C^* liquid crystals.

From the above measurements, we conclude that chiral organosiloxane LMM mesogens have potentially very interesting physical properties. The single component material studied exhibited a high tilt (~36°) room temperature ferroelectric S_C^* phase with a P_s of 17 nC cm^{-2} at 25°C. This P_s is similar to typical optimized room temperature eutectic mixtures. Clearly P_s could be increased by replacing the 2-methylbutyl chiral group by one of higher polarity. Equally the chiral centre could be coupled further from or closer to the first aromatic ring to alter P_s, tilt angle and helix pitch. We have started work in this direction and results for the new compounds [21] and the chiral/achiral mixture [22] will be reported in detail soon. The switching times of the organosiloxane S_C^* compounds are similar to other LMM organic materials and P_s and θ_t are, respectively, only weakly dependent and independent of temperature. Such behaviour, which would in a practical device obviate the need for temperature compensation in the drive waveform or electronics, appears to be the result of the first order isotropic to smectic C* phase transition. We have shown good alignment is possible by combining surface forces and applied low frequency AC fields at a temperature just below the I–S_C^* transition. This alignment is maintained at lower temperatures and we are currently measuring bistability as a function of sample thickness and mechanical shock. The ease with which these organosiloxane materials may be aligned and the weak temperature variation of the physical parameters does raise the question as to whether pitch compensation at the N* to S_A transition, with the concomitant strong dependence of P_s and θ_t on temperature in the S_C^* phase, is the best route for obtaining stable aligned ferroelectric materials suitable for many complex applications. The constancy of the tilt angle is particularly useful for fixing the optical polarizer axis with respect to the switched states thereby maintaining good optical contrast as a function of temperature. Other homologues with different tilt angles are currently being synthesized to produce optimum tilt angles of 22·5° suitable for birefringence devices. Equally, using these high tilt, fast response (or low viscosity) materials, we are re-examining the dye–guest ferroelectric mode [23, 24], which has the advantage of requiring only one input polarizer, thereby giving at least twice the optical throughput of a comparable birefringence device.

In summary, the incorporation of the flexible siloxane moiety into a LMM mesogenic structure has led to a new class of S_C^* compounds that show fast switching times yet have highly ordered structures reminiscent of SCLCP materials. Such 'pseudo' polymers would appear to be a good compromise between LMM organic and SCLCP materials.

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