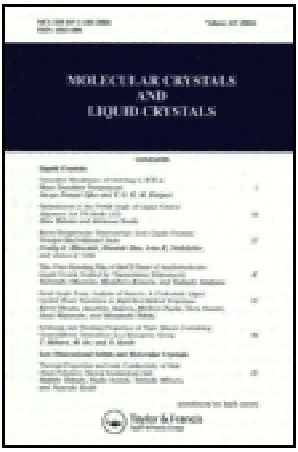

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# Comparison of Mesomorphic Behaviour and Electro-Optic Properties of Ferroelectric Mesogens With and Without Disiloxane End-Groups

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# COMPARISON OF MESOMORPHIC BEHAVIOUR AND ELECTRO-OPTIC PROPERTIES OF FERROELECTRIC MESOGENS WITH AND WITHOUT DISILOXANE END-GROUPS

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Abstract Low molar mass liquid crystals with phase properties similar to polymers may be obtained by the addition of a disiloxane tail to an organic mesogen. We present a comparison of the properties of two chiral mesogens (based on the 4-((S)-(+) 2-Methylbutanoyloxy)phenyl 4-(9-decenyloxy)benzoate and 4-((2S)-2-Chloro-3-methylbutanoyl)phenyl 4'-(9-decenyloxy)benzoate moieties) with and without a pentamethyl disiloxane tail and with their vinyl-terminated analogues. We show a general decrease in transition temperatures, and a widening of the mesophase range in the disiloxane-substituted materials due to a suppression of the crystallisation temperature. The phases exhibited are modified, with a tilted smectic-C phase favoured on substitution of the disiloxane tail, eliminating the smectic-A phase found in the unsubstituted mesogen; this gives high tilt angle (28-36°) single mesophase materials. We summarise the electro-optic properties of a series of the disiloxane-substituted materials, which show low viscosity (~500mPas) and moderate spontaneous polarisation (20-150nCcm$^{-2}$) across the range of materials, and show their variation with temperature. We demonstrate the variations of these properties with varying alkyl spacer length, alkyl tail length and changing chiral end-group.

## INTRODUCTION

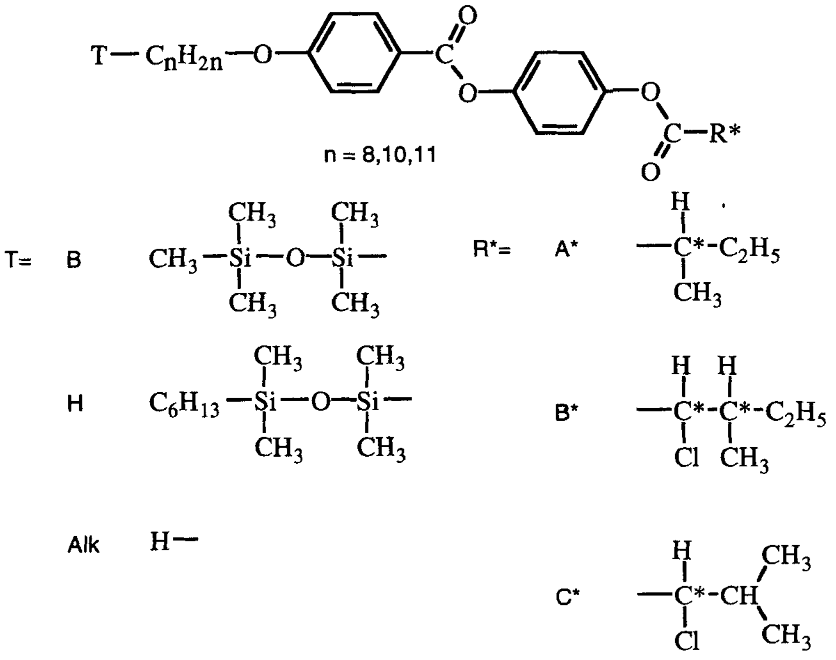
We have previously described[1-3] the properties of several disiloxane-substituted ferroelectric liquid-crystalline materials derived from the 4-((S)-(+) 2-Methylbutanoyloxy)phenyl 4-(9-decenyloxy)benzoate and 4-((2S)-2-Chloro-3-methylbutanoyl)phenyl 4'-(9-decenyloxy)benzoate moieties, and have shown that they have properties distinct from those of conventional low molar mass (LMM) materials, whilst having similarities to siloxane-based side-chain liquid-crystal polymer (SCLCP) systems[4-6]. The increased layer stability in smectic systems of SCLCPs and the broadening of their mesophase ranges by the lowering of the crystal/glass transition temperature has useful technological consequences, but is offset by the adverse effect on response times of reorientation to electric fields. The viscosity, which scales as a power law of the molecular weight, gives reorientation times several orders of magnitude slower than in their LMM analogues under the same conditions. To overcome this we have synthesised molecules with a short siloxane tail, lowering the molecular weight of the molecules while hopefully retaining the intermolecular interactions and lowering the crystallisation temperatures. This is indeed observed[7], and may be explained in terms of a separation of the siloxane moiety from the mesogen in the layer structure of the mesophase, the agglomeration of the siloxane units giving a lower energy conformation structure.

In the SSFLC configuration the dominant parameters governing the reorientation time in the moderate-field regime[8,9] are the spontaneous polarisation $P_S$, the applied electric field, and the viscosity coefficient for Goldstone-mode motion[10] $\gamma$, giving a characteristic response time $\tau = \gamma / P_S E$. It is of interest to examine how these parameters $P_S$, $\gamma$ and the tilt angle of the smectic-C mesophase, $\theta$, vary with changing temperature. This has been extensively done with ferroelectric mesophases with a second-order transition into the phase, but comparatively little work has been done on materials with first-order phase transitions. To study this we have measured these parameters as a function of temperature for a group of related compounds with the general formula $C_nR^*T$, as shown in Figure 1, where $C_n$ refers to the number (n) of methylene spacers separating the tail moiety T from the common mesogenic core, and R* refers to the chiral endgroup.

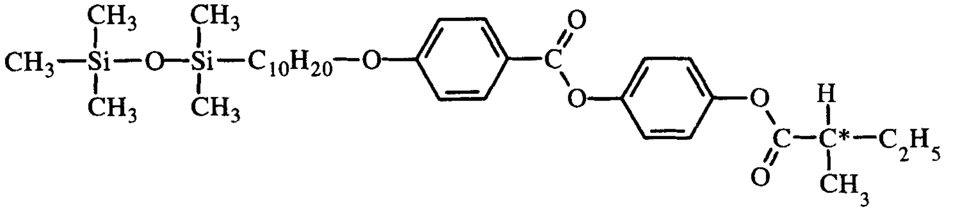
## PHASE IDENTIFICATION

The textures and transition temperatures of the mesophases were studied by polarising optical microscopy using an Olympus BH2 polarising microscope linked to a Mettler FP82 Hot Stage and temperature controller (see Table I). $C_8A^*B$ exhibits only an unstable monotropic $S_C^*$ transition, which is observed for a short time in thin films (~4μm) before crystallising. The transitions are slightly affected by the cell boundaries both with and without surface aligning agents, depressing crystallisation temperatures in thinner cells. The chiral $C_{10}A^*B$, $C_{10}B^*B$ and $C_{10}C^*B$ all exhibit one enantiotropic $S_C^*$ phase. X-ray data[7] confirms a single enantiotropic smectic-C phase in the S-enantiomer $C_{10}A^*B$, the racemate $C_{10}A^{(\pm)}B$, the $C_{10}B^*B$ and the $C_{10}C^*B$. The mesophase supercools somewhat, in some cases crystallising at less than -5°C depending on sample type (for instance whether in electro-optic cell, DSC cell or capillary tube); hence an accurate measure of melting/freezing point is difficult. Unusually, the natural texture of the smectic phase formed on cooling from the isotropic liquid is always that of batonnets coalescing into focal-conic fans, with the more commonly observed Schlieren texture never being observed[11]. On crystallisation, the texture of the mesophase is not preserved, giving rise to a complex paramorphotic texture on heating.

$C_nR^*T$



For instance, $C_{10}A^*B$:



$C_{10}A^*$, $C_{10}A^{\pm}$

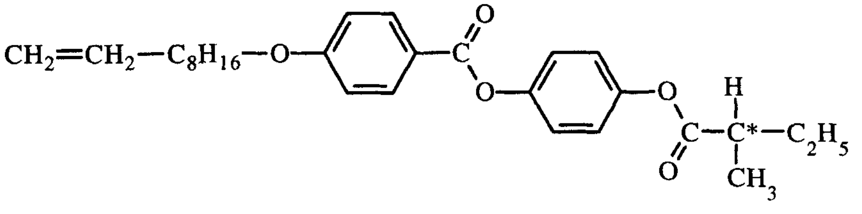


FIGURE 1 Molecular structures of materials studied

Thermal analysis of the LMM chiral and achiral organosiloxane materials was also performed using a Perkin-Elmer DSC7 machine linked to a data station with heating and cooling rates of 5 °Cmin$^{-1}$ and 10 °Cmin$^{-1}$. These results confirmed the optical observations, as shown in Table I.

Organosiloxanes

| Material | $K\text{-}S_C^*$ /°C | $S_C^*\text{-}I$ /°C |
|---|---|---|
| $C_8A^*B$ | - | (34.9) |
| $C_{10}A^*B$ | -5 | 50.7 |
| $C_{11}A^*B$ | -4.5 | 47.3 |
| $C_{10}B^*B$ | -3 | 47.1 |
| $C_{10}C^*B$ | 0 | 47.1 |
| $C_{11}C^*B$ | 1 | 47.5 |
| $C_{10}A^*H$ | 2 | 32.3 |
| $C_{10}A^{\pm}B$ | -1 | 49.5 |
| $C_{10}C^{\pm}B$ | 10 | 47.9 |

Hydrogenates

| Material | $K\text{-}S_C^*$ /°C | $S_C^*\text{-}S_A$ /°C | $S_A\text{-}I$ /°C |
|---|---|---|---|
| $C_{10}A^*Alk$ | (12.5) | 41.0 | 51.0 |

TABLE I Phase transition temperatures of the materials studied. Brackets indicate a monotropic transition. The vinyl materials $C_{10}A^*$ and $C_{10}A^{\pm}$ have only unstable mesophases.

## ELECTRO-OPTIC PROPERTIES

The principal configuration in which materials with ferroelectric liquid-crystalline mesophases are studied is the surface-stabilised ferroelectric liquid crystal (SSFLC) cell[12], in which the layer structure of the chiral smectic phase is perpendicular to the cell glass boundaries, with a homogenous aligning agent on the glass surfaces to promote uniform director structure and to unwind the bulk helical director conformation, giving a hopefully bistable system. Our materials were studied in this configuration in purpose-made glass cells, giving sample thicknesses of approximately 3.5µm (supported with glass spacer beads). Indium Tin Oxide layers on the internal cell glass surfaces were used to apply electric fields, and these were coated with a rubbed polyimide layer for homogenous alignment, the rubbing directions on either surface being antiparallel. The electrode area was 5x5mm$^2$. Pretilt of the molecules from the surface was ascertained to be small[13] (<2°). Upon cooling the materials do not naturally align on the polyimide, and give rise to the same textures as without alignment agents, that is, a focal-conic texture. We found no discernible electro-optic response in either of the racemates $C_{10}A^{\pm}B$ or $C_{10}C^{\pm}B$, while their enantiomer analogues gave a readily discernible optical change with an applied field, the extinction positions on the focal-conic fan backs changing according to the polarity of the field. Goldstone-mode switching was confirmed by the use of a continuously varying applied field, confirming the presence of ferroelectricity in all of the enantiomers with mesophases.

The SSFLC configuration requires good alignment for an accurate determination of its properties. This is usually produced by slow cooling in materials for which the chiral smectic-C phase underlies a nematic and smectic-A phase, such that the director configuration and layer structure formed respectively in these phases is preserved, though stressed, on cooling into the lower phase. The alignment produced is usually only quasi surface-stabilised in that the director profile winds up after any applied electric field is removed, so that there is no bistability; this occurs for materials in which the pitch length of the bulk director helix structure is not appreciably greater than the sample film thickness. Our materials do not possess a nematic mesophase, and so we therefore applied an alternating square-wave electric-field ( ~ 100 Hz @ ~ 10 V$\mu$m$^{-1}$) to the sample film while cooling slowly through the transition, which gives rise to an electro-hydrodynamic (EHD) instability[14]. Charge liberated from the electrodes is moved back and forth, disturbing the forming batonnets, and allowing them to take up an homogenous conformation. The resulting cell generally has good layer alignment, with a moderately low density of zig-zag defects[2,3] in accord with the antiparallel low pretilt conditions within the cell[15]. However, defects remaining within the cells mean that this structure is generally not bistable for more than ~ 0.1 s. Alignment may also be achieved by poling in a strong DC electric field, and the alignment obtained is similar. However, charge separation within the cell is greater, and the danger of electrical breakdown due to ionisation is high. The materials are nevertheless robust, and withstand field strengths of over 30 V$\mu$m$^{-1}$ without observable degradation. They are also stable to normal environmental conditions, and do not require any special handling. On application of a sufficiently strong electric field (>~ 5 V$\mu$m$^{-1}$) the zig-zag defects disappear, and we contend that the systems are thus in a voltage-stabilised near-bookshelf geometry. The electro-optic measurements made here assume the existence of this structure.

## Tilt Angles

The variation of tilt angle with temperature was measured in the SSFLC configuration, and is shown in Figure 2 for the organosiloxane enantiomers, and in Figure 3 for the hydrogenate $C_{10}A^*Alk$. Measurements were made with field applied, and the tilt angle was taken as half the angle between extinction orientations, between crossed polarisers, corresponding to opposite polarity fields. Saturation was verified by varying the field strength, and taken as true because of the low pretilt. The material $C_8A^*B$ does not possess a stable mesophase, but it was still possible to obtain a measure for the tilt angle, of approximately 38° near to the isotropic transition, which does not vary with temperature as far as could be measured before crystallisation.

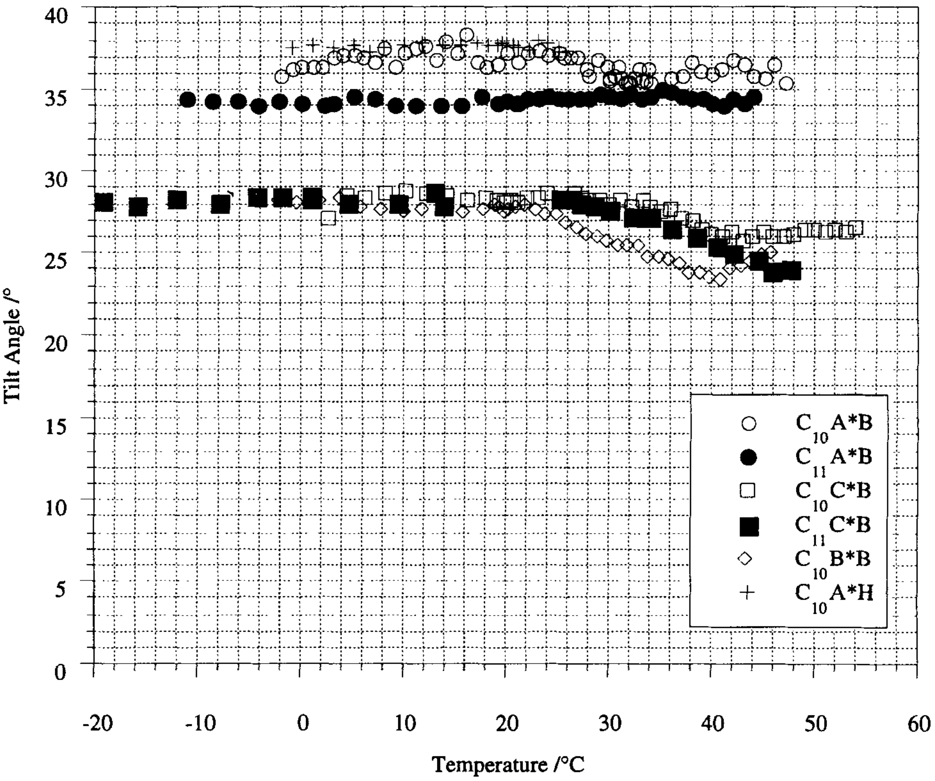


FIGURE 2 Tilt angles in the ferroelectric phases of the organosiloxane materials. Their variation with temperature is negligible. Error bars are not shown for clarity - A typical error on each point is ±0.5°.

Spontaneous Polarisation And Rotational Viscosity

We employed the current-pulse method[16], which measures the charge liberated on applied electric field polarity reversal. The accuracy of this method is dependent upon there being a small dielectric effect, which may be quantified by the parameter[16] $r$,

$$r = \frac{\Delta\varepsilon\varepsilon_0 E_0 \sin^2\theta}{P_S} << 1. \qquad (1)$$

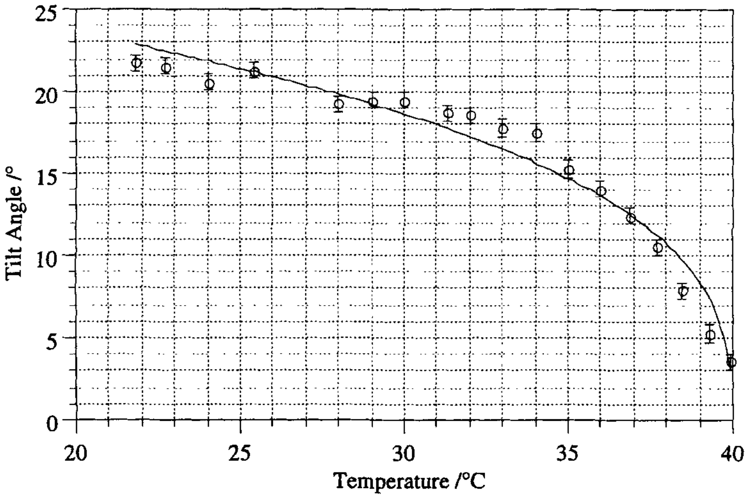


FIGURE 3 Tilt angles in the ferroelectric phase of $C_{10}A^*Alk$, showing the conventional second-order Landau form for the temperature dependence of the tilt angle.

The coefficient of viscosity may also be measured from the shape of the current pulse peak, using the relation[16]

$$\gamma = \frac{AP_S^2 E_m}{I_p^m \sin^2 \theta}, \tag{2}$$

provided that the switching is co-operative rather than defect-mediated[8,9] ($P_S$ is the spontaneous polarisation, $\theta$ the tilt angle, $E_m$ and $I_p^m$ the field and polarisation current at the peak of the pulse, and $A$ the switching area). This was verified by microscopic observation. This method was employed for the organosiloxane enantiomers and the hydrogenate $C_{10}A^*Alk$. The polarisation results are shown in Figures 4 and 5, with a typical viscosity curve shown in Figure 6 for $C_{10}B^*B$. The other organosiloxanes had similar shaped temperature dependencies for the rotational viscosity.

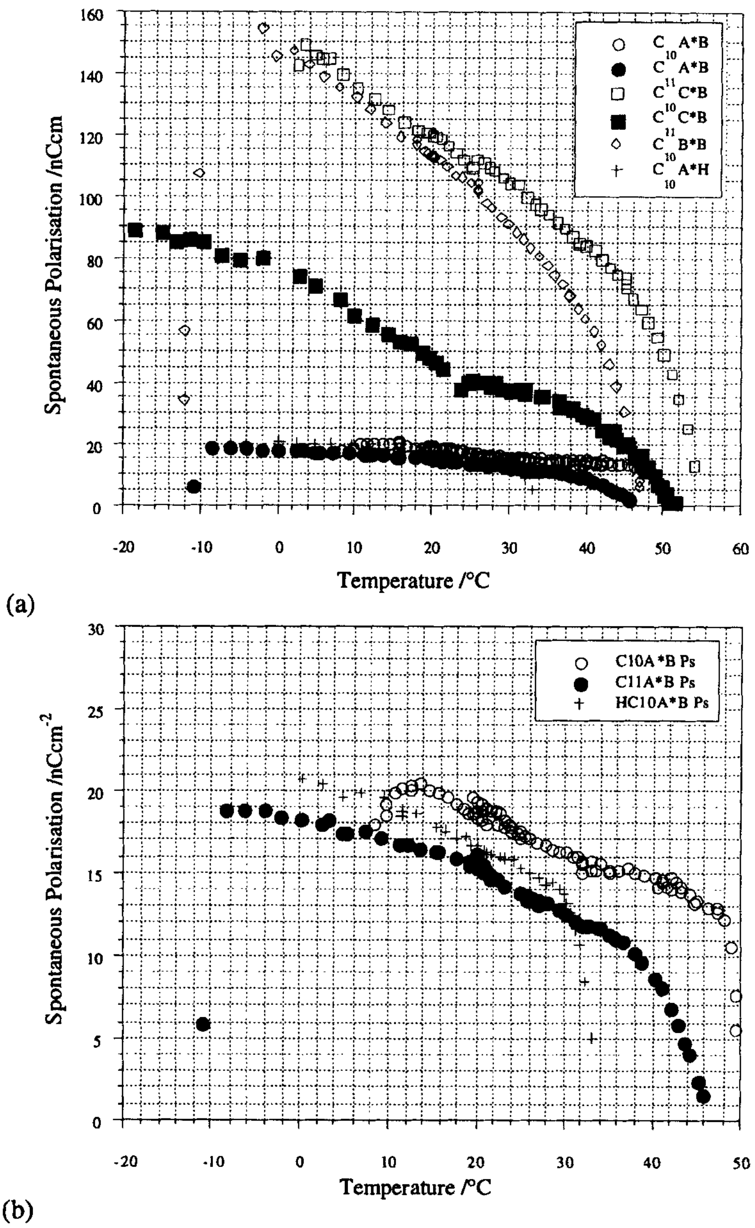


FIGURE 4 (a) Variation of spontaneous polarisation with temperature for the organosiloxane liquid crystals. The ratio $P_S/\theta$ is clearly not a constant. (b) is a magnified view of the non-chlorine containing materials. Error bars are again not shown for clarity, but are typically 10% of the value of $P_S$.

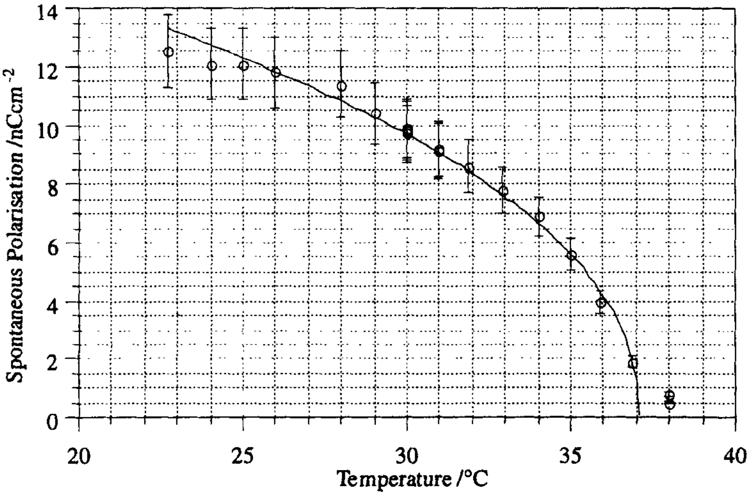


FIGURE 5 Spontaneous polarisation in C10A*Alk, showing the same second-order form as for the tilt angle.

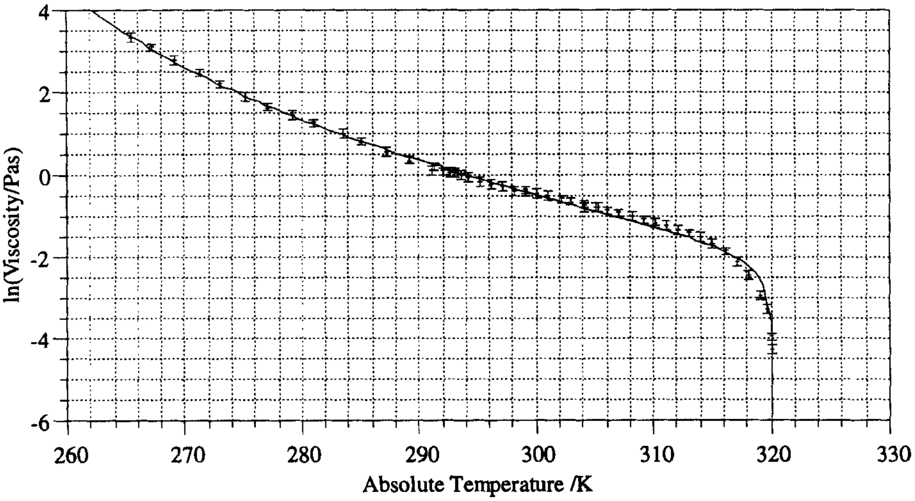


FIGURE 6 Variation of viscosity with temperature for C10B*B. $\gamma$ diverges at low temperatures as the transition temperature into the crystalline phase is approached, whilst the order parameter $S$ dominates the high-temperature behaviour.

## ANALYSIS OF RESULTS

It is clear from Figure 2 that the tilt angle is not an order parameter for the phase, as is common for first-order materials[17,18], although this is worth pointing out as in the more usual second-order transitions it is, for instance in the hydrogenate material in this work (Figures 3 and 5). The variation of the spontaneous polarisation (Figure 4) must therefore be connected with some other ordering in the mesophase, presumably some orientational order parameter which also induces some biaxial ordering within the mesophase. This warrants further theoretical study. However, we may gain some insight into this ordering from the variation of the rotational viscosity. Figure 6 shows that the Arrhenius form for its temperature variation is inadequate; however, several authors have put forward descriptions of the behaviour of the rotational viscosity of nematics[19-25]. Following the work of Bock et al.[19], we postulate that the behaviour in these first-order ferroelectric phases is similar to that observed in nematics, derived to explain the divergence from Arrhenius behaviour at high and low temperatures. The viscosity is then written as

$$\gamma = \zeta^2(T)V(T) \tag{3}$$

where $\zeta$ is some order parameter. We do not know the form of this parameter, although since the spontaneous polarisation of the organosiloxanes varies continuously to zero at the transition into the isotropic phase, we may write an expainsion of it to first order as

$$\zeta = \left(1 - \frac{T}{T_C}\right)^{\beta} \tag{4}$$

where $T_C$ is some critical temperature related to the onset of the ferroelectric phase transition, and so should be close to it. $V(T)$ is the dependence of Vogel's equation related to the glass transition ( $V(T) = e^{\left({}^{B}\!/_{T-T_G}\right)}$), so that equation (3) becomes

$$\gamma = A\left(1 - \frac{T}{T_C}\right)^{2\beta} e^{\left(\frac{B}{T-T_G}\right)} \tag{5}$$

where $A$ and $B$ are constants and $T_G$ is a glass temperature. A typical data fit is shown in Figure 6, and from this it may be seen that the behaviour of the viscosity coefficient is well-modelled by this equation. The activation energy for rotation may be calculated from equation (5), and at the transition is given by

$$E_A = R\left(\frac{d\ln\left(\gamma/\zeta^2\right)}{d(1/T)}\right)_{T_C} = \frac{RBT_C^{\,2}}{\left(T-T_G\right)^2} \tag{6}$$

These values are given in Table II.

| Material | Activation Energy /kJmol$^{-1}$ |
|---|---|
| $C_{10}A^*B$ | 14 ± 2 |
| $C_{11}A^*B$ | 15 ± 2 |
| $C_{10}B^*B$ | 32 ± 4 |
| $C_{10}C^*B$ | 20 ± 3 |
| $C_{11}C^*B$ | 35 ± 4 |
| $C_{10}A^*H$ | 29 ± 4 |

TABLE II Activation energies for rotation in the organosiloxane materials calculated from equation (6).

## DISCUSSION

The goodness of fit of the viscosity data to the form of equation (6) indicates that the behaviour of the rotational viscosity in these smectic mesophases is similar to that observed in nematics, although the activation energies obtained are somewhat smaller, those for nematics being generally ~ 30 kJmol$^{-1}$. This may be due to many factors, and as yet no conclusion may be drawn. A detailed analysis of both first-order and second-order smectic maerials of the type described will be presented at a later date[26].

A comparison of the activation energies obtained allows us to draw some conclusions as to the effect of functional groups upon the dynamic behaviour of these systems. It seems that the activation energy increases with chiral end-group size in the order $C_{10}B^*B>C_{10}C^*B>C_{10}A^*B$, and that addition of a methylene group to the spacer chain also increases this energy. There is an anomaly in that addition of a methylene group to the C*B molecule increases the activation energy by a much greater amount than in A*B, and this is reflected in a very different behaviour for the spontaneous polarisation. This would suggest that the molecular packing is upset by the addition of this group and is different between the two materials $C_{10}C^*B$ and $C_{11}C^*B$, although this is to be confirmed by X-ray analysis and is at present a tentative statement. Interestingly, comparing $C_{10}A^*B$ to $C_{10}A^*H$ shows that the addition of a hexyl chain to the end of the molecule has a much larger hindering effect upon the rotation than expected from the viscosity measurements, which show them to have the same viscosity at a particular temperature. This would suggest that the hexyl chains are present in the same region as the polar groups in the microphase-separated layers discerned from X-ray analysis[7]. However, these are conjectures which must be verified by further work. These results suggest that these materials have considerable potential for electro-optic devices.

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