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Structural characterization of mono- and di-mesogenic organosiloxanes: The impact of siloxane content on biphenyl benzoate systems

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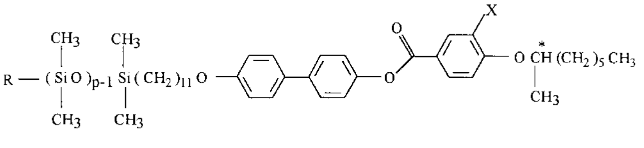
A structural characterization of two series of ferroelectric low molar mass organosiloxanes is described. X-ray and dilatometry studies have been used to determine the impact of variations in mono- or di-mesogen architecture, halogen substitution and siloxane content on the mesophase structure and thermal behaviour. All of the compounds exhibit smectic C* mesophases with high tilt angles. Bromo substituted compounds are consistently found to exhibit higher tilt angles than their fluoro analogues, and a strong odd–even effect in melting temperature is observed for the dimesogenic bromo series.

1. Introduction

Ferroelectric liquid crystalline organosiloxanes are reported to exhibit the electro-optic properties of low molar mass systems while maintaining the mechanical advantages of their polymeric analogues [1–6]. The combination of fast response and mechanical stability has shown potential for the fabrication of rugged displays [7–9]. Lateral substitution of a classical calamitic mesogenic unit (paraffinic chain plus aromatic core) and its attachment terminally to a limited number of dimethysiloxy groups (typically 1–10 repeats) can produce low T_g, low viscosity, and monodisperse materials. The bulk structures of such systems are characterized by a microphase separation of the three constituent moieties into separate regions due to the different characters of the paraffinic, aromatic and siloxane moieties [10–12]. This behaviour results in the formation of distinct sublayers, which in turn superimpose to form the lamellar liquid crystalline phase. The final structure depends on the relative influence of each of the constituent groupings. Studies have previously been carried out to determine the impact of siloxane content and mono- or di-mesogen substitution in orthogonal lamellar (SmA) phases [10, 11]. This article is concerned with the impact of such variations on tilted lamellar, chiral (SmC*) structures, to complement work already published on the influence of variations in the chiral end group [12].

2. Materials

The chemical structure of the organosiloxanes is shown below. In the following, the structures are referred to as p/X or $X/p/X$, where p denotes the number of silicon atoms in the siloxane group, and X indicates the type of halogen substituent. The $p=2$–5 derivatives contained monodisperse siloxane moieties. The higher homologues were polydisperse in this respect, exhibiting a bimodal distribution with peaks at $p=5$ and 11 of varying ratios, and the two samples studied had an average siloxane content of 7 and 9. The synthesis of the two series has been described in separate articles [6, 13], along with their thermal and electro-optical characteristics.



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Monomesogens $R=CH_3$
$X=Br$ $p=2,3$
$X=F$ $p=2$
Dimesogens $R=$alkoxybiphenyl benzoate
$X=Br$ $p=2, 3, 4, 5, 7, 9$
$X=F$ $p=3, 5, 7, 9$

The thermal behaviour of the compounds is summarized in table 1. All of the materials exhibited mesomorphic behaviour. The large increase in siloxane content is seen to have minimal impact on the clearing temperatures of the materials. However, a strong odd–even effect in melting temperature is observed for the dimesogenic bromo series: compounds with an even number of siloxane groups demonstrate melting temperatures 30° higher than the odd membered homologues, which in turn exhibit mesophases over a 60°C temperature range. The monomesogenic derivatives demonstrate ferroelectric switching with high spontaneous polarization ($\mathbf{P}_s \sim 95\,\mathrm{nC\,cm^{-2}}$) and optical tilt angle (~45°). For both the bromo and fluoro series, these values [6, 13] are almost temperature independent. The bimesogenic compounds are found to be predominantly ferroelectric, apart from the Br/3/Br, F/3/F and F/5/F homologues which show only antiferroelectric behaviour. The $\mathbf{P}_s$ and tilt angles were weakly dependent on temperature and both decreased with increasing spacer length [13].

3. Experimental

Powder X-ray diffraction patterns were recorded as a function of temperature using a Guinier-type camera with a bent quartz monochromator ($\mathrm{CuK}_{\alpha 1}$ radiation, $\lambda = 1{\cdot}54$ Å), an INSTEC hot-stage (±0·01°C) and an INEL curved position-sensitive gas detector. Samples were housed in sealed Lindemann glass capillaries. For selected temperatures, patterns were recorded on film using a Phillips PW-1009 generator. Dilatometry measurements were made using a dilatometer constructed in-house [14]. Specific volume measurements were obtained on stepwise heating and cooling between 25°C and the isotropic phase at a rate of 0·1°C every 2 mins. Molecular modelling was carried out using Insight II software (Version 2.3.0, Biosym Technologies), on a Silicon Graphics Indigo workstation.

Table 1. Thermal behaviour for the mono- and di-mesogenic organosiloxanes (°C on cooling; values in brackets indicate a broad transition observed within the mesophasic region).

X/*p*/*X*	Solid–meso	Meso–iso
2/Br	34·3 (47·6)	84·3
3/Br	40·2 (46·3)	87·1
Br/2/Br	70·4	102·3
Br/3/Br	40·0	107·5
Br/4/Br	71·5	98·3
Br/5/Br	38·6	102·9
Br/7/Br	33·0	93·6
Br/9/Br	32·8	98·1
2/F	34·8	86·8
—	—	—
—	—	—
F/3/F	51·2	121·2
—	—	—
F/5/F	46·9	115·0
F/7/F	37·5	84·2
F/9/F	46·3	111·3

4. Results and discussion

4.1. *X-ray diffraction*

X-ray patterns for all the materials were consistent with the formation of a fluid lamellar mesophase stable over a wide temperature range. A single Bragg peak was seen at small angles corresponding to the smectic layer spacing. At wide angles, two diffuse bands were observed corresponding to the disordered lateral arrangement of the molecules within the smectic layer: one band arises from combined contributions from the paraffin chains in a liquid-like conformation and the aromatic cores (~4·6 Å), and the second, more diffuse band, probably corresponds to the siloxane moieties (~7 Å) [15, 16]. On cooling to ambient temperature, all the compounds underwent a transition into a lamellar solid. In the small angle region, an increase in lamellar spacing was observed, along with the appearance of a second and/or third order peak. In the wide angle region, a small increase in the mean spacing of the mesogenic groups (to ~4·8 Å) occurred, and a peak at 4·1 Å emerged, thought to arise due to the development of ordering in the mesogenic sublayer.

The lamellar periodicity for each of the compounds in the mesophase, along with the corresponding molecular lengths estimated by molecular modelling, are given in table 2. The spacings were only weakly dependent on temperature across the whole mesomorphic range for all the compounds, in agreement with optical tilt angle measurements [6, 13]. As expected, the smectic period

Table 2. Smectic period (*d*) in the mesophase and molecule length (*L*) of the mono- and di-mesogenic organosiloxanes.

X/*p*/*X*	*d*/Å, Br	*d*/Å, F	*L*/Å
2/*X*	35·0	38·0	46
3/*X*	39·0	—	48
X/2/*X*	36·0	—	84
X/3/*X*	33·2	34·4	86
X/4/*X*	33·9	—	89
X/5/*X*	35·6	39·1	92
X/7/*X*	42·4	49·8–46·1	97
X/9/*X*	44·8–46·7	45·8–47·3	103

increased with molecular length for the monomesogens, and for the dimesogens where $p \geqslant 3$. The smectic periods for the dimesogenic $p=3$ compounds were smaller than for their monomesogenic analogues as would be expected, and as has also been observed for three component cyanobiphenyl–paraffin–siloxane systems [10, 11]. However, the Br/2/Br homologue had a lamellar spacing which was similar to that of its monomesogenic analogue, and higher than that of the neighbouring higher member of the dimesogenic homologous series. The bromo compounds consistently exhibited a smaller layer spacing than their fluoro analogues, implying that bromo substitution induces a higher tilt in the aromatic sublayer.

4.2. *Dilatometry*

Dilatometry measurements were carried out on three compounds to determine the impact of the addition of a dimethylsiloxane group (2/Br to 3/Br) and of a mesogenic group plus paraffin spacer (3/Br to Br/3/Br). At the solid–mesophase transition, all three materials exhibited a small (~1%) and reversible volume change, indicating the existence of a non-crystalline solid which was consistent with the X-ray data and the waxy appearance of the compounds at ambient temperature. On clearing, each of the materials showed the expected small, reversible volume jump. The 2/Br derivative exhibited an additional first order volume change at 44°C (~1%; figure 1). No change was seen in the X-ray diffraction pattern, optical texture or tilt angle at this temperature, but a clear enthalpy peak is seen by DSC ($\Delta H \sim 2{\cdot}4\,\mathrm{J\,g^{-1}}$) [6]. It is proposed that the transition corresponds to a rearrangement of the siloxane moieties. A similar peak is seen in the DSC for the other monomesogenic bromo derivative (3/Br), but not for the dimesogenic homologues, nor for the fluoro compounds.

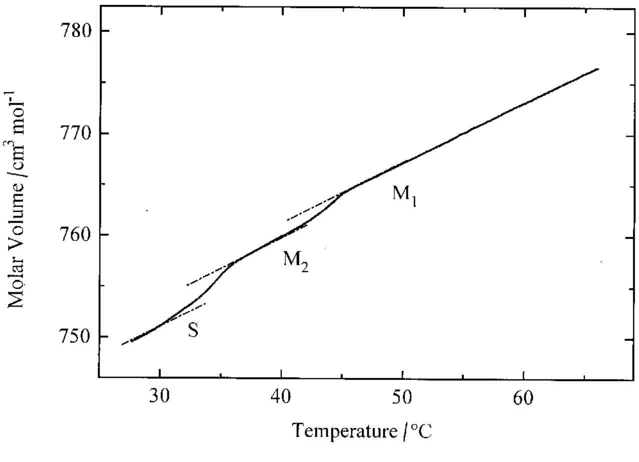

Figure 1. Detail from molar volume data for the 2/Br derivative on cooling, showing mesophase–mesophase and mesophase–solid transitions.

Within a fluid phase, the molar volume varies linearly with temperature, such that $V(T) = V_0(1 + \alpha T)$, where V_0 is the molar volume at 0°C and α is the relative thermal expansion coefficient. The values of V_0 and α calculated from the 45–70°C region of the mesophase of each compound, along with the molar volumes at 60°C, are compared in table 3. The values for thermal expansion are typical of those found previously for fluid smectic phases [17]. On making the assumption of additivity of partial molar volumes of the constituent parts of the molecule, the volume occupied by a single dimethylsiloxane group at 60°C can be estimated to be $60\,\mathrm{cm^3\,mol^{-1}}$. This value is smaller than that calculated for a repeat unit in an isotropic polydimethylsiloxane chain ($77\,\mathrm{cm^3\,mol^{-1}}$) [18], which is to be expected due to the constraints placed on the end groups in a chain subsequently attached to another moiety. Using the same method, the volume occupied by a mesogenic group plus paraffin spacer is estimated at $\sim 590\,\mathrm{cm^3\,mol^{-1}}$.

4.3. *Structural model*

The fluid lamellar phases formed by all the compounds exhibit layer periodicities significantly less than their molecular lengths, indicating a tilted smectic structure which is consistent with the optically observed tilt angle and electro-optic switching (SmC*). As stated above, the different amphiphilic characters of the constituent parts of molecules of this type result in a segregation of the aromatic, paraffinic and siloxane moieties into distinct sublayers within the lamellar phase. In order to understand more fully the phase structure, it is useful to obtain the value for a molecular area (S) in the mesophase, which can be estimated from dilatometry and the X-ray data. The three constituent parts each have satisfactorily to occupy the calculated molecular area, and this should give an insight into the packing within each distinct sublayer and thus into the overall structure formed. The molecular area for the monomesogenic compounds was calculated to correspond to the surface occupied by two molecules in the smectic layer, due to the two-sided symmetry of the smectic layers ($S = 2V/Nd$, where V is the molar volume, N is Avogadro's number and d is the smectic period). For the dimesogenic compound, the molecular area of a single molecule was calculated ($S = V/Nd$). Values of the molecular areas for three compounds at 60°C are given in table 3.

For the monomesogenic compounds, the calculated S is more than twice the molecular area of the aromatic core: $\sigma_{\mathrm{ar}} \sim 22$–$24\,\text{Å}^2$ [17], which with the bromo substitution is estimated by molecular modelling to rise to $\sim 27\,\text{Å}^2$. These figures suggest a monolayer arrangement

Table 3. Values of molar volume at 0°C (V_0) and relative thermal expansion coefficient (α) in the SmC phase, together with molar volume (V) and molecular area (S) at 60°C, for selected mono- and di-mesogenic organosiloxanes.

$X/p/X$	V_0 cm^3 mol^{-1}	$\alpha \times 10^{-4}$ °C^{-1}	V at 60°C cm^3 mol^{-1}	S at 60°C Å^2
2/Br	737·9	8·0	773·0	73
3/Br	795·7	7·9	833·4	71
Br/3/Br	1359·5	7·7	1422·1	71

of tilted aromatic groups with a tilt angle of $\cos^{-1}(2\sigma_{\mathrm{ar}}/S) \sim 42^\circ$, which is consistent with the optically measured tilt angle [6]. For a linear paraffin chain, molecular areas (σ_{par}) may vary between 20–40 Å^2 depending on the chain conformation, while areas from 29 Å^2 have been estimated for a branched chain [12], again consistent with a monolayer arrangement of aromatic cores (figure 2). The molecular area of a dimethylsiloxane polymer chain (σ_{sil}) is approximately 43 Å^2 [19], which is considerably smaller than S and suggests a partially bilayered arrangement of the siloxane end groups. The degree of interdigitation, ρ, in the siloxane sublayer will depend on the tilt angle of the siloxane moieties which, within the current model, is not precisely defined due to the wide range of conformations available to the siloxane chains: a higher limit occurs if the siloxane groups are on average orthogonal to the layers, giving $\rho \cong S/\sigma_{\mathrm{sil}} - 1 \sim 0{\cdot}7$, and a lower limit can be defined when the siloxane groups adopt a similar angle to the aromatic cores, giving $\rho \sim (\cos 42^\circ)^{-1} - 1 \sim 0{\cdot}3$.

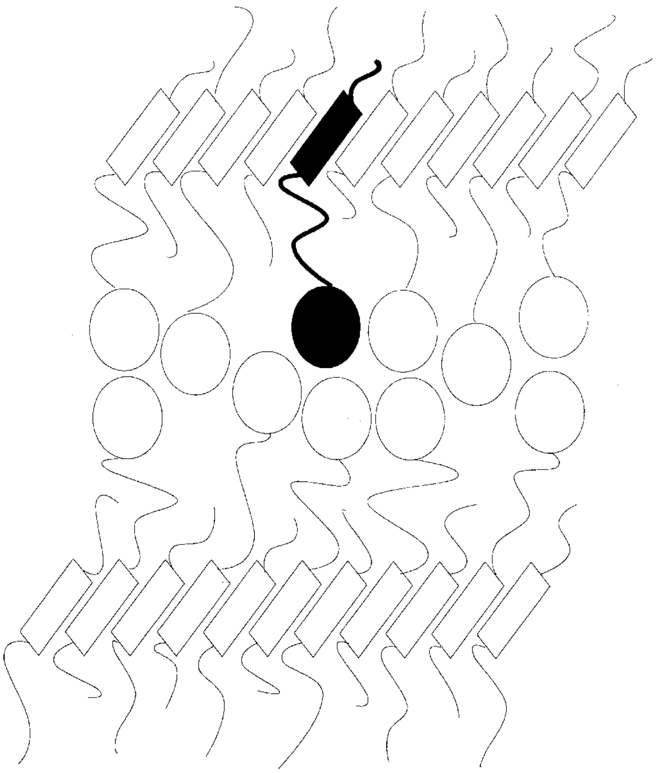

Figure 2. Schematic representation of the tilted smectic structure formed by the monomesogenic organosiloxanes. A partial bilayer of siloxane groups (ellipses) is flanked by mesogenic moieties packing to form tilted monolayers (aromatic cores represented by rectangles and paraffin chains represented by wavy lines).

For the dimesogenic system, the calculated S is again more than twice the molecular area of the aromatic core, giving a slightly smaller tilt angle of $\sim 40^\circ$ which follows the trend observed optically. As detailed above, the pair of paraffin chains per molecular area is consistent with this monolayer arrangement of aromatic cores. The ratio of S to σ_{sil} is also such that the orthogonal siloxane cross-section is considerably smaller than the molecular area; however in the dimesogen system it is not possible to model a simple interdigitation as in the monomesogenic case. Two solutions present themselves, in both of these the siloxane chain does not lie fully extended, but instead bends back on itself, running in part parallel to the smectic layer, thus increasing the transverse area occupied. Then, either the two mesogenic groups are splayed producing the tilted analogue to the SmA structure previously reported for dimesogenic organosiloxanes incorporating cyanobiphenyl moieties [11] (figure 3 (*a*)), or the siloxane fully bends back on itself as shown in figure 3 (*b*). Similar values were obtained on energy minimization of an isolated molecule in the splayed and bent configurations. Further studies are being carried out to determine the most suitable model.

5. Conclusions

The influence of variations in mono- or di-mesogen architecture, halogen substitution and siloxane content on the mesophase structure and thermal behaviour of low molar mass biphenyl benzoate organosiloxanes has been presented. All of the compounds demonstrate smectic C* mesophases with high tilt angles. A large increase in siloxane content is seen to have minimal impact on the clearing behaviour of both homologous series, but a strong odd–even effect is observed in melting temperature. The bromo derivatives consistently exhibit a smaller layer spacing, and thus a larger tilt angle, than their fluoro analogues. A structure consisting of an aromatic monolayer and partially interdigitated siloxane bilayer is presented for the monomesogenic derivatives, while two potential structures are proposed to resolve the siloxane packing difficulties in the bimesogenic compounds.

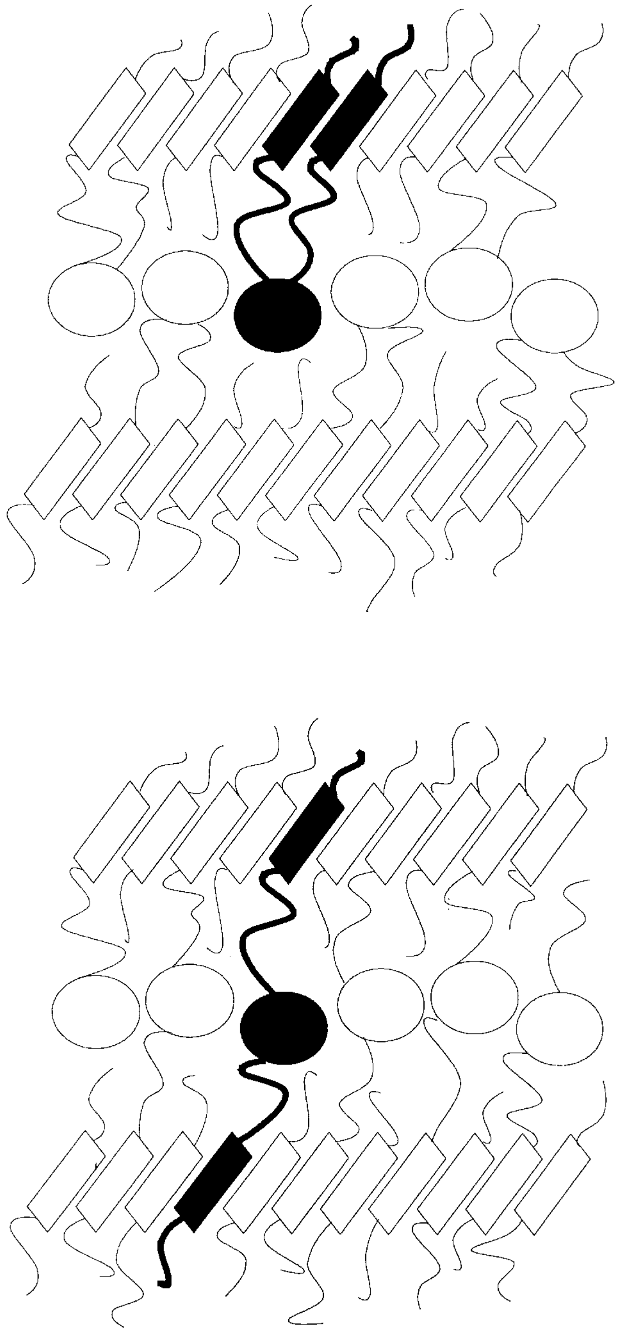

Figure 3. Schematic representation of the two tilted smectic structures proposed for the dimesogenic organosiloxanes. See figure 2 for key.

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