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Enhanced thermal response of the $S_{A_{d1}}$ layer thickness in highly fluorinated thermotropic liquid crystals

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X-ray studies of a homologous series of rod-shaped liquid crystal molecules with one tail perfluorinated and the other protonated, reveal large decreases in the smectic A layer spacing with increasing temperature. These materials form unique dimer phases in which the smectic layer spacing is dependent on the length of the perfluorinated tail and independent of the length of the protonated tail. The chain statistics of the perfluorinated tail significantly influence the thermal expansion coefficient since the length of the fluorinated tail defines the smectic layer spacing. Thermal expansion coefficients for the layer spacing observed here are negative and nearly an order of magnitude greater than for typical protonated rod-shaped thermotropic liquid crystals in the SA phase.

1. Introduction

In this paper we examine the influence of fluorination on the thermal contraction of the layers in the smectic A phase with increasing temperature, in a new class of rod shaped liquid crystal-forming molecules having a perfluoroalkyl tail on one end and an ordinary alkyl tail on the other—see table 1 for structure. Several homologous series of these highly fluorinated materials have been produced [1–4] for evaluation in display devices. These types of material present a unique system based on molecules having sterically, chemically, and kinetically different ends.

Thermal expansion is anisotropic in liquid crystal phases and particularly pronounced in these highly fluorinated materials. While the overall volume of a liquid crystal sample increases with increasing temperature [5, 6], the layer spacing in the smectic A_1 phase typically remains constant or shrinks [7–10]. This effect has been attributed to the increased disorder of the tail groups, which are aligned normal to the layers in the S_{A_1} phase, with increasing temperature [10]. Expansion or contraction of the smectic layers is of particular importance in display devices, where very long range (several cm^2) alignment of the smectic layers is required. Variation in layer thickness can lead to the production of defects [11] which greatly diminish the performance of a device.

From X-ray scattering experiments we find that all homologues in table 1 exhibit negative thermal expansion coefficients of the S_A layers, significantly larger than those

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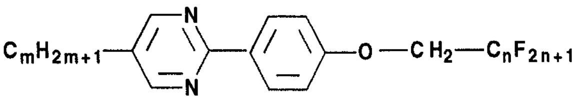
Table 1. Phase transition temperatures (°C) for the various homologues of the 5-*n*-alkyl-2-[4-*n*-(1,1-dihydroperfluoroalkoxy)phenyl]pyrimidine series. Phase transition temperatures were determined by differential scanning calorimetry (DSC) on cooling from the isotropic phase at 5°C min^{-1}. All phases were also observed upon heating except for the S_C phase of 10/3 (monotropic). The liquid crystal phases were identified by polarizing optical light microscopy. For simplicity the homologues are referred to as *m*/*n* where *m*(*n*) is the number of carbons in the hydrocarbon (fluorocarbon) tail, see the structure diagram.



m/*n*	*X*	←	S_C	←	S_A	←	I
6/7		50		56		133	
7/7		54		67		125	
8/7		71		80		117	
9/7		71		85		112	
10/7		75		87		104	
10/5		47		73		84	
10/3		36		52		64	

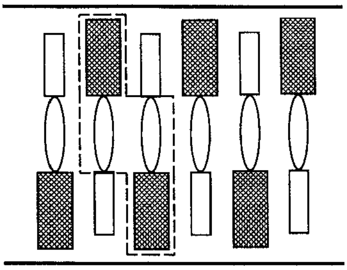


Figure 1. Antiparallel alignment of nearest neighbours. Cores are represented as ovals. Fluorinated and protonated tails are represented as shaded and open rectangles, respectively. The box surrounding the dimer pair indicates the structural unit which defines the smectic layer. Note that the protonated tails do not contribute.

previously observed for the S_{A_1} phase. Furthermore, the magnitude of this effect increases with increasing perfluorinated tail length. We will show that the chain statistics of the perfluorinated tail significantly influence the thermal expansion coefficient. Our previous structural study [12] indicates that: (i) in the smectic A (S_A) and C (S_C) phases the homologues in table 1 are organized into antiparallel pairs, i.e. with fluorinated and protonated moeties adjacent ($S_{A_{d1}}$ and $S_{C_{d1}}$ phases); (ii) the smectic layer spacing is strongly governed by the fluorinated tail length and independent of the protonated tail length; (iii) the molecules are registered relative to one another along their lengths. In the $S_{A_{d1}}$ phase, the molecules are oriented normal to the layer boundary with the length of the fluorinated tails in adjacent dimer pairs defining the layer thickness, see figure 1.

2. Experimental

Aligned, homeotropic sample were prepared on microscope slides cleaned with acetone. The substrates were placed on a hot plate, and the liquid crystal melt allowed to spread in the isotropic phase. The samples were then quickly transferred to a preheated single-stage scattering oven (stability ≈ ± 50 m°C, $T_{\max}$ 115°C) in order to maintain the smectic phase. It was found that thin sample films break up into droplets if cooled into the crystal phase and reheated. This flow-thinning technique produces a homeotropically aligned film approximately 20 μm thick (3 samples were measured using a Zeiss light sectioning microscope) with a nearly uniform thickness over a $1 \times 2\,\mathrm{cm}^2$ area.

X-ray scattering experiments were conducted on a two circle diffractometer with a rotating anode (Rigaku RU-300) CuK_α source, a bent graphite monochromator, slit collimation and a Bicron scintillation detector. The X-ray spot size at the sample position was 0·275 mm × 2·0 mm in cross-section. The instrument resolution was 0·066°, full width at half height (FWHH) of a 2θ scan through the main beam.

Our scattering geometry was such that the samples were oriented normal to the floor and to the scattering plane of the instrument. With the detector in the main beam ($2\theta = 0$) and the sample just out of it, the plane of the substrate was oriented parallel to the beam with the diffractometer θ axis centred in the plane of the substrate. Alignment was completed by translating the sample normal to the beam until the beam intensity was halved. The detector (2θ) and sample (θ) orientations were scanned independently in order to locate and maximize the intensity of the (001) Bragg peak. At maximum intensity θ was reset to 1/2 of 2θ Bragg. The samples were heated to just below the smectic A to isotropic phase transition (temperature limited by the scattering oven) and held there for 15 min in order to stabilize the system. Data were collected as $\theta/2\theta$ scans (step sizes of 0·0125°/0·0025°, respectively) as the samples were cooled from the $\mathrm{S_A}$ to the crystal phase.

3. Results and discussion

The smectic layer spacing as a function of temperature for the individual homologues is shown in figure 2 (*a*), (*b*). All samples studied had monochromator like alignment with $0{\cdot}04° \leq \mathrm{FWHH}_{(001)} \leq 0{\cdot}06°$, which is less than the instrument resolution (FWHH = 0·066°), and a θ mosaic of 0·11° (FWHH).

All samples demonstrate a negative thermal expansion coefficient (α) in the $\mathrm{S_{A_{dl}}}$ phase (dashed lines in figure 2 (*a*), (*b*), table 2), where

$$d_\mathrm{A} = d_\mathrm{AC}(1 + \alpha(T - T_\mathrm{AC})), \qquad (1)$$

and d_A is the $\mathrm{S_{A_{dl}}}$ layer spacing, T is the temperature, and d_AC and T_AC are the layer spacing and temperature at the $\mathrm{S_{A_{dl}}}$ to $\mathrm{S_{C_{dl}}}$ phase transition. The negative thermal expansion coefficient is attributed to an increase in the thermal fluctuations (disorder) in the liquid crystal tails [9]. The smectic layer spacing decreases with increasing temperature through two coupled mechanisms: The liquid crystal tails spend less time in an extended conformation as the temperature is increased, which is accompanied by an increase in the lateral pressure between neighbouring tails. The first effect is directly seen in the 10/*n* series for which $|\alpha|$ increases with increasing fluorinated tail length (recall that the smectic layer spacing is strongly dependent on the length of the fluorinated tail), see figure 3. The second effect is less obvious. Increased lateral pressure forces the molecules further apart with an accompanying shrinkage in the smectic layer thickness in order to fill space. This explains why $|\alpha|$ increases as the length

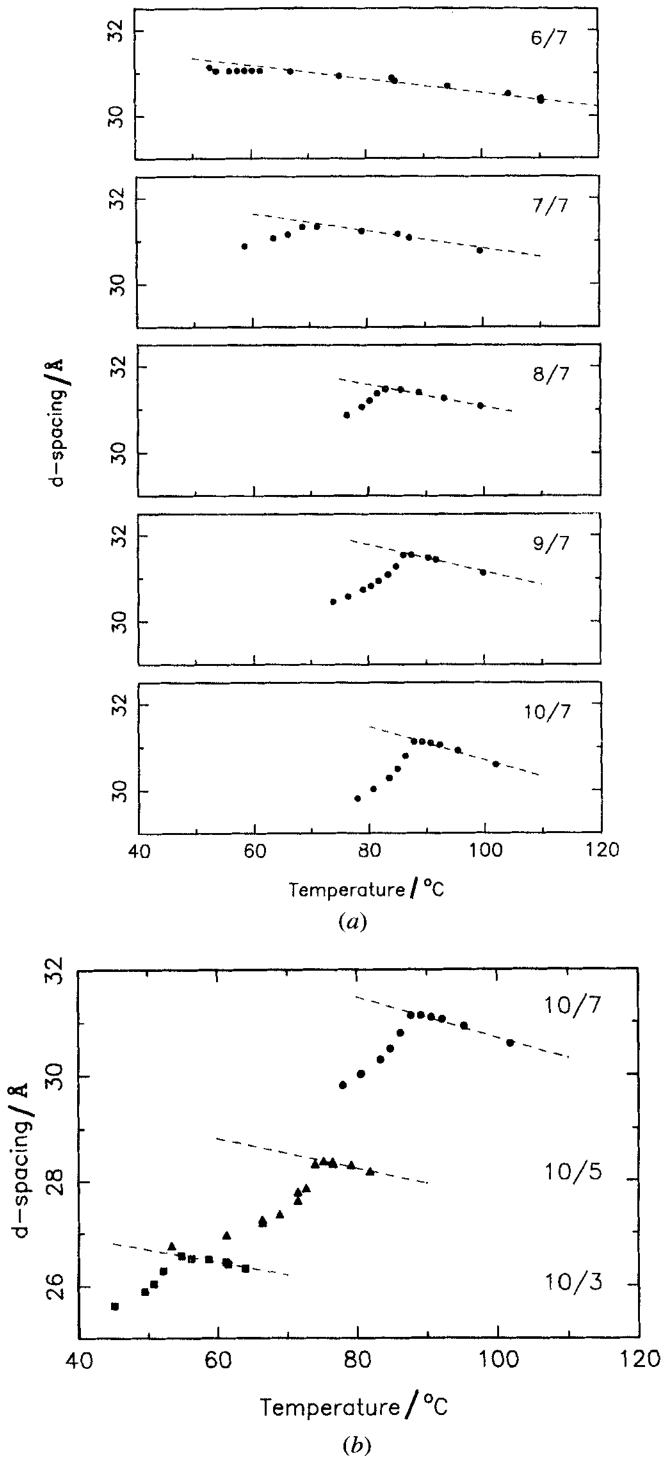


Figure 2. Layer spacing as a function of temperature for the homologue of table 1. (*a*) *m*/7 homologues. (*b*) 10/*n* homologues. The dashed lines are linear least squares fits to the S_A data. The resultant fitting parameters and thermal expansion coefficients are listed in table 2.

Table 2. Summary of experimental data. Data extracted from the plots presented in figure 2(*a*)(*b*). S_A–S_C transition temperature (T_{AC}), smectic layer spacing at the S_A to S_C transition (d_{AC}), molecular length (l) (as calculated for the lowest energy conformation using MOPAC [13]), slope and intercept of straight line fit to the S_A data (dashed line), and thermal expansion coefficient (α) for the various homologues. Errors given in parentheses are in the last significant figure unless a decimal point is given. the relative errors on T_{AC}, d_{AC}, and l are estimated to be 0·2°C, 0·2 Å, and 0·2 Å, respectively.

m/n	T_{AC}/°C	d_{AC}	l/Å	Slope/ (10^{-2} Å °C)	$d(T=0)$ (Å)	$\alpha/10^{-4}$ °C^{-1}
6/7	≈59·0(2)	31·1(2)	30·1(2)	−1·6(1)	32·1(1)	−5·1(4)
7/7	70·0	31·4	31·3	−2·0(2)	32·8(2)	−6·4(8)
8/7	82·8	31·5	32·7	−2·5(4)	33·6(4)	−7·9(1·3)
9/7	86·4	31·6	33·9	−3·1(5)	34·3(4)	−9·8(1·6)
10/7	87·9	31·2	35·3	−3·9(4)	34·6(4)	−12·5(1·4)
10/5	75·2	28·5	32·6	−2·9(6)	30·6(4)	−10·2(2·0)
10/3	53·4	26·6	30·0	−2·4(4)	27·9(2)	−9·0(1·6)

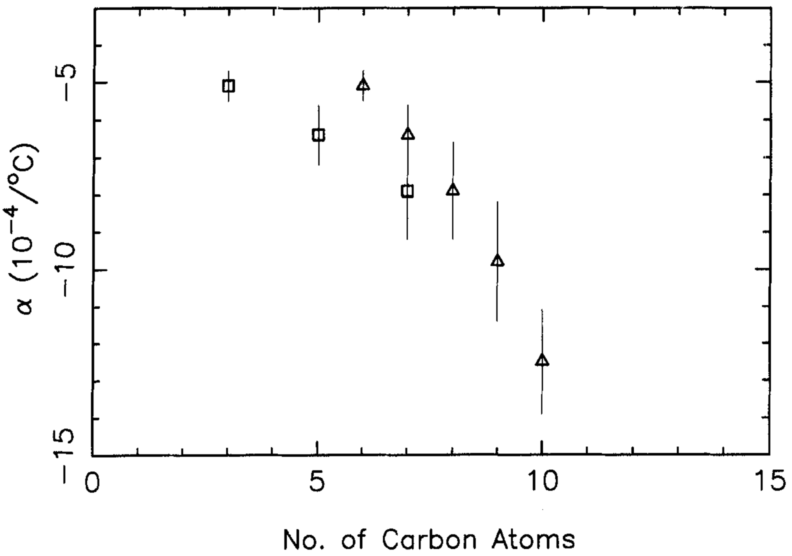


Figure 3. Thermal expansion coefficient (α) versus the number of carbon atoms in either tail. Triangles-fixed fluorocarbon tail length, *m*/7 series. Boxes-fixed hydrocarbon tail length, 10/*n* series. Error bars are ± σ from table 2.

Table 3. Comparison of the number of *gauche* to the number of *trans* conformers for polyethylene (PE) and polytetrafluoroethylene (PTFE) at 25 and 100°C (total of 100 bonds).

	$\Delta\varepsilon$/cal/mol$_{-1}$	N_g/N_t(25°C)	N_g/N_t(100°C)	Bonds converted
PE [15]	500	46/54	50/50	4
PTFE [16]	1200	21/79	29/71	8

of the hydrocarbon tail increases in the *m*/7 series (see figure 3), even though the hydrocarbon tail length has little effect on the smectic layer spacing, see table 2.

The negative thermal expansion observed in the $S_{A_{d1}}$ phase continues into the $S_{C_{d1}}$ phase, but is in general masked by the large layer shrinkage associated with the tilt of the director in the $S_{C_{d1}}$ phase as the temperature is reduced. Due to the changing molecular order of the $S_{C_{d1}}$ phase, the thermal expansion coefficient need not have the same value or functional dependence on temperature as in the $S_{A_{d1}}$ phase. A sufficiently large negative thermal expansion coefficient could compensate for the layer shrinkage associated with the $S_{C_{d1}}$ phase.

The negative thermal expansion coefficients observed in this homologous series are nearly an order of magnitude greater than the largest reported for protonated thermotropic liquid crystals [10]. This is a direct consequence of the chain statistics of the perfluorinated tail, which defines the smectic layer spacing as in figure 1. Conformational analysis (MM2′) on the central bond in perfluoro-*n*-butane and *n*-butane yields the expected three local minima, one *trans* and two degenerate *gauche* conformations [14]. At equilibrium, the ratio of the number of *gauche* to *trans* conformations is dependent on the energy separating these states ($\Delta\varepsilon$) and the temperature by

$$N_g/N_t = 2\exp(-\Delta\varepsilon/(RT)). \qquad (2)$$

Table 3 shows the ratio of the number of *gauche* to *trans* conformers calculated from equation (2) at 25 and 100°C. We have chosen experimentally determined values of $\Delta\varepsilon$ from polymer systems [15, 16] as these more accurately reflect the liquid crystal environment than the $\Delta\varepsilon$ used in the MM2′ calculations [14]. We draw two conclusions from table 3: (i) for a given temperature the perfluorinated chain is more extended (larger number of *trans* conformers) than the protonated one, and (ii) the length of a perfluorinated chain changes more rapidly (larger number of bonds converted from *trans* to *gauche* conformation) than for a protonated one for a given temperature change. This latter effect, coupled with our observation that the homologues studied here form dimer phases in which the length of the fluorinated tail defines the layer spacing and neighbouring molecules are registered along their long axis, explains the large negative thermal expansion coefficient observed.

The S_{A_d} and S_{A_2} phases demonstrate negative thermal expansion coefficients an order of magnitude greater than those reported here [17–19]. However, in the S_{A_d} phase, the registration of neighbouring molecules relative to one another along their lengths changes with temperature. In the S_{A_2} phase, two layers (4 tail groups) contribute to the thermal expansion coefficient of the smectic layers.

In conclusion, we have shown that the thermotropic liquid crystal homologues studied, with one tail perfluorinated and the other protonated, demonstrate enhanced temperature dependence of the S_A layer thickness due to the coupling of dimer ordering within the layer and the temperature dependent chain statistics of the perfluorinated tail. In addition, the effects of thermal disorder of the two tails can be separated.

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