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The structural basis of transitions between highly ordered smectic phases in semifluorinated alkanes

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The semifluorinated alkanes $F(CF_2)_{10}(CH_2)_9H$ and $F(CF_2)_{10}(CH_2)_{11}H$ both undergo a reversible transition between tilted smectic phases above room temperature as demonstrated previously for $F(CF_2)_{10}(CH_2)_{10}H$. The transformation on cooling is achieved in two stages: an increase in molecular tilt relative to the layer normal, followed by a change in the molecular interdigitation within each layer. The extent of complete transformation is sensitive to temperature and time, due to strains occasioned by the accompanying volume change, and because the second stage requires significant molecular translations. Characterization of the transformation is possible by transmitted light microscopy, supplemented by X-ray diffraction.

1. Introduction

Mixtures of low molecular weight hydrocarbons $H(CH_2)_nH$ and perfluorinated hydrocarbons $F(CF_2)_mF$ are significantly non-ideal (e.g. often immiscible). Structurally, these materials are very different: at room temperature, hydrocarbon chains exist as a planar zig-zag series of $-(CH_2)-$ units (as in polyethylene), while perfluorinated chains $-(CF_2)-$ favour a conformation based on a 15/7 helix (as in polytetrafluoroethylene). When these two units are bound covalently to produce a semifluorinated hydrocarbon $F(CF_2)_m(CH_2)_nH$, the resultant compounds may exhibit structural transitions between layered phases at temperatures below the clearing point [1–3]. For the case of $m = n = 10$ (perfluorodecyl decane, represented here as F10H10), it has been shown (4) that these transitions are between tilted smectic liquid-crystalline phases. This compound represents an unusual structure for a mesogenic molecule, since it does not contain the phenyl group or multiple bonds that are characteristic of the rigid moiety in most conventional liquid crystals. Also, in the presence of simple hydrocarbon solvents, the semifluorinated molecules form organized gel-like structures [3, 5] which are primitive (non-ionic and non-polar) surfactants.

The reversible liquid crystal–liquid crystal transition in F10H10 has been described in some detail [4], together with the structure above and below this transition. However, it was recognized that structural studies of this compound, in which the fluorinated and hydrogenated stems have closely similar lengths, might lead to a model that is not generally applicable to other homologues. In the present contribution, we report the results of structural studies conducted on the related compounds F10H9 and F10H11. We show that the model developed previously for the transformation in F10H10 can be applied successfully to these compounds as well.

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2. Synthesis of materials

The semifluorinated alkanes F10H9 and F10H11 were prepared by conventional means, involving addition of perfluorodecyl iodide to 1-nonene (for F10H9) or 1-undecene (for F10H11) and subsequent dehalogenation of the iodide-containing intermediate with zinc in ethanolic HCl. The intermediate and product were purified easily by simple distillation and the product was determined to be > 99 per cent pure by gas chromatographic analysis in each case. Further details regarding synthesis can be obtained from [4].

3. Experimental

3.1. *Optical microscopy*

Microscopy was performed on specimens held between a conventional rectangular glass microscope slide and cover slip, using a Carl Zeiss (Jena) Amplival polarizing microscope. Microstructures (textures) were observed at elevated temperatures by using a Linkam 26-THM-600S heating/freezing stage and 26-PR-600 controller, which provided for a variety of heating/cooling rates as well as for viewing under isothermal conditions.

3.2. *X-ray diffraction*

Small angle X-ray scattering data and wide angle X-ray diffraction patterns were recorded simultaneously in transmission on a flat plate Warhus camera under vacuum. Specimens were held in Lindemann glass capillaries having an internal diameter of 1 mm and a wall thickness of 0·01 mm. The temperature of the specimen holder was maintained to better than 0·1°C by means of an external oil bath. The radiation was CuKα, and the specimen-to-film distance was 139·3 mm. This camera length conveniently allows diffraction at small and large angles to be recorded on a single 10 cm by 8 cm film.

4. Results and discussion

For both compounds, we write LC1 and LC2 to denote the liquid-crystalline phases, with LC2 referring to the phase which is stable at lower temperatures. In accord with our previous work on F10H10, we use the term transition temperature to denote the temperature above with LC1 forms on heating and below which LC2 forms on cooling. The term melting will refer specifically to the formation of an *isotropic* phase from LC1 on heating.

4.1. *Optical microscopy of LC1*

As-synthesized F10H9 responds plastically to pressure applied between a microscope slide and cover slip. When heating at 2°C/min, it becomes markedly more plastic above *c*. 45°C (though no specific change in texture is observed), and melts at 58·7°C to give a clear isotropic fluid. F10H11 behaves similarly, melting at 63·4°C. Specimens form a distinctive liquid-crystalline texture on subsequent cooling. An undercooling of a few degrees is necessary in each case, the exact value being sensitive to the cooling rate. As was observed for F10H10, and reported in detail [4], the texture is characteristic of a smectic G or J liquid crystal, i.e. a structure which is based on a C-centred monoclinic unit cell in which molecules are packed in pseudo-hexagonal fashion and *tilted* relative to the layer normal.

4.2. *Optical microscopy of LC2*

The mosaic texture of LC1 undergoes a transformation on further cooling. The scale of the new texture is sensitive to cooling rate, becoming finer as the cooling rate increases. Even if specimens are observed with an oil immersion objective (necessarily at room temperature, since the working distance of this type of lens cannot accommodate the heating stage), it is not possible to identify a specific texture for LC2. Also, equilibrium conditions for the transformation cannot be defined easily, since the timescale over which the transformation occurs is highly sensitive to temperature. For example, more than an hour is required for the transformation in F10H11 at 55°C, but the process takes only a few seconds at room temperature.

As is the case with F10H10, the individual domains in LC2 have a well-defined orientation of habit relative to that of the parent domains. We specifically observe that there are *two* orientations in which LC2 develops from any LC1 domain. On reheating, the outlines of the original domains of LC1 (as formed during the most recent cooling from the isotropic state) are still preserved, but the domains of LC2 are replaced by striations running normal to the length of the original LC1 domains. This is consistent with our previous model for F10H10, according to which [4] the tilt in LC2 can be resolved into a smectic G-like component (i.e. a tilt towards the midpoint of a hexagon face in the basal plane of the unit cell) and a smectic J-like component (i.e. a tilt towards a vertex in the basal plane). In LC1, the tilt consists of only one of these components. The existence of phases with tilts intermediate to the extreme case represented by smectics G and J has been predicted recently on theoretical grounds [6–7].

The approximate magnitudes of the tilt angles in phases LC1 and LC2, and the thickness of the smectic layers, are deduced from X-ray diffraction.

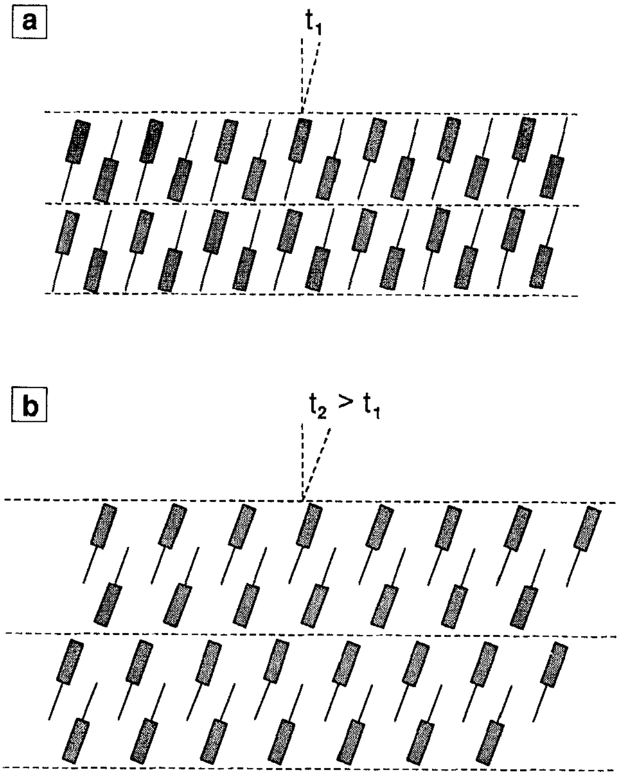
4.3. *X-ray diffraction*

The *d*-spacings calculated from the diameter of the rings as measured directly from film are listed in the table. Data were collected above and below the LC1–LC2 transition. The largest *d*-spacing is assigned to the layer thickness. By extending the arguments used previously for F10H10 [4], it is straightforward to show that molecules of F10Hn have an approximate length of $13{\cdot}7(3) + 1{\cdot}25n$ Å. We postulate that a void exists between adjacent layers (since LC1 deforms under shear, and the individual layers are not sufficiently correlated to give rise to *hkl*-type reflections), and that the void size must exceed 1·42 Å (the F–F bond distance). For both F10H9 and F10H11, it then follows that the component of layer thickness that is occupied by molecules is slightly smaller than the length of a molecule, which necessitates that the

d-Spacings for F10Hn.

Sample	Temperature/°C	Observed *d*-spacing/Å					
F10H9	53·0	26·1	13·5–14·5	4·7–4·8			
	21·0	35·1	21·5	13·5–14·5	5·4	5·0	4·7
F10H11	58·0	28·7	13·5–14·5	4·7–4·8			
	21·0	35·8	24·2	13·5–14·5	5·3	4·9	4·7

Data were obtained from as-synthesized material heated to the temperature indicated. Random errors are limited by the accuracy of measurements read from X-ray film. The largest spacings are accurate to ±0·5 Å; the smallest ones are accurate to ±0·1 Å.



(*a*) Antiparallel packing model for molecules in LC1. (*b*) Packing model for partially interdigitated molecules in LC2. In both cases, fluorinated segments are indicated by the heads, and hydrogenated segments by the tails. The structures are viewed in a section that contains the layer normal and the direction ⟨100⟩. t_1 and t_2 indicate molecular tilt angles relative to the layer normal.

molecules be tilted relative to the layer normal. The *approximate* tilts for F10H9 and F10H11 are 9° ± 4° and 7° ± 4°, respectively. These small angles are comparable to the value 5° – 7° determined by small angle X-ray scattering for the LC1 phase of F10H10 [4]; they are also consistent with qualitative estimates made from optical interference figures, which are biaxial. The antiparallel packing model shown schematically in figure (*a*) accommodates the tilts just discussed, the structural conclusions derived from optical microscopy, and the results [2] of calculations of non-bonded interaction energies. Furthermore, it is consistent with the structure of the LC1 phase in F10H10 [4] and also in F12H12 [2].

The layer spacing in LC2 (35·1 Å for F10H9 and 35·8 Å for F10H11) in both cases is greater than the molecular length, but less than three times the length of the longer segment of the molecule. We proceed by assuming that the model shown in figure (*b*) is applicable, since (*a*) it minimizes the change in tilt and the relative displacement of adjacent molecules required to achieve the transformation from LC1, (*b*) by placing hydrogenated segments in closest contact, in the middle of each layer, the model leaves least space for possible interpenetration of layers, and (*c*) it is consistent with the model proposed previously [4] for F10H10. Molecular tilts in the LC2 phase of F10H9 and F10H11 are therefore calculated as being 29° ± 3° and 33° ± 3°, respectively.

A peak is detected at 21·5 Å for F10H9, representing slightly less than 2/3 of the layer spacing just described for the LC2 phase. We interpret this smaller distance as the full layer spacing that would result if the molecules adopt the *tilt* characteristic of LC2, but retain the relative molecular *displacements* characteristic of LC1. The fact that 21·5 Å is *less* than 2/3 d_{001} for LC2 follows from the shorter length of the hydrogen segment relative to the fluorocarbon segment. A similar interpretation can be given to the peak at 24·2 Å in F10H11.

These results, together with our previous observations on F10H10, suggest that LC2 forms from LC1 in two stages. First, the tilt angle increases. Adjacent molecules then undergo a change in relative interdigitation, analogous to the relative displacement of protein molecules that achieves contraction or relaxation in muscle [8]. The second stage, requiring greater molecular mobility, is likely to be sluggish in comparison with the first, leading to the observed sensitive dependence of the transformation on temperature and time. Below the transformation temperature, the samples consist of a two-phase mixture of partially and fully transformed material. Our model for the transformation between the LC1 and LC2 phases predicts a large accompanying volume change. This must result in a significant coherency or misfit strain [9]. Coherency/misfit strain relaxation therefore must contribute to the time dependence of the transition. Qualitatively the volume change is easy to observe when specimens held in capillaries are heated through the transformation temperature during our diffraction experiments. Dilatometric measurements made on cooling, as a function of volume fraction of fully transformed material, would provide a useful test for our model.

Given the limited number of diffraction maxima, the diffuse nature of some of the peaks, and the likely two-phase structure below the transition temperature, it is difficult to make unambiguous unit cell assignments for LC1 and LC2. Dilatometric measurements of the transition will help to reduce this ambiguity.

5. Conclusions

(1) The semifluorinated alkanes F10H9 and F10H11 both undergo a reversible transition between tilted smectic liquid-crystalline phases.

(2) The transition on cooling (i.e. from LC1 to LC2) occurs in two stages. The first involves an increase in the angle at which molecules are tilted relative to the layer normal. The second involves a change in the relative interdigitation of molecules.

(3) Our model for the transition does not depend on the hydrocarbon and fluorocarbon segments having closely similar lengths.

(4) The transformation is associated with a significant volume change. Measurements of this change as a function of fully transformed volume fraction would provide additional information for determining the LC1 and LC2 unit cells.

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