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Transitions to Liquid Crystalline Phases in Tri-Block Oligomers $F(CF_2)_n(CH_2)_m(CF_2)_nF$

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Using transmitted polarized light microscopy, we identified liquid crystalline behavior in the tri-block semifluorinated alkanes $F(CF_2)_{12}(CH_2)_8(CF_2)_{12}F$, $F(CF_2)_{10}(CH_2)_{10}(CF_2)_{10}F$ and $F(CF_2)_{12}(CH_2)_{12}(CF_2)_{12}F$. All three compounds exhibit mosaic textures (smectic B) on heating to within 0.4°C of the temperature at which an isotropic melt is formed. The smectic B-isotropic transition is reversible. Crystallization is accompanied by the formation of a fine sub-texture within the smectic B domains. The sub-texture has a well-defined orientation relative to the habit of the parent domains, suggesting that molecules develop a tilt relative to the layer normal. Both the scale of the sub-texture and the temperature at which it begins to form depend on the cooling rate, indicating a significant kinetic barrier to the accompanying molecular rearrangement.

Keywords: Fluorocarbon, mesophase, mosaic texture, semifluorinated alkane, smectic, tilt

INTRODUCTION

In previous publications[1–3] we have described liquid crystalline phases of di-block semifluorinated alkanes $F(CF_2)_n(CH_2)_mH$ and the related iodine-containing derivatives $F(CF_2)_{10}CH_2CHI(CH_2)_{n-2}H$. Two characteristics of these families of compounds stimulated our interest. Firstly, the rigid, elongated structure necessary for mesophase formation is provided by the *conformation* and not the configuration of the molecules; the multiple bonds or aromatic rings typical[4] of the rigid moiety in most liquid crystals are absent. Secondly, because they are bonded chemically, the component hydrocarbon and fluorocarbon segments are forced to coexist in a single phase. Simple mixtures of fluorocarbon and hydrocarbon oligomers would rapidly separate into two phases.[5]

The availability of tri-block semifluorinated alkanes $F(CF_2)_n(CH_2)_m(CF_2)_nF$ enables us to extend our studies to cases where the molecules do not have distinguishable "head" and "tail" ends. This simplifies the number of distinguishable

molecular ordering schemes. Initial studies[6] did not reveal the presence of any liquid crystalline phases in the tri-block materials. However, as in the case of the di-block materials, hot-stage light microscopy is particularly suited to detecting liquid crystalline phases. The light microscope provides direct visual evidence of the liquid crystalline order, and the heating stage enables sensitive and accurate temperature control.

EXPERIMENTAL

Materials

Studies were conducted on the following three materials: $F(CF_2)_{10}(CH_2)_{10}(CF_2)_{10}F$, $F(CF_2)_{12}(CH_2)_8(CF_2)_{12}F$ and $F(CF_2)_{12}(CH_2)_{12}(CF_2)_{12}F$. For convenience, these compounds will be represented below by the abbreviated notations F10H10F10, F12H8F12 and F12H12F12 respectively. Typical syntheses are given in Reference 6.

Transmitted polarized light microscopy

Specimens ($\leq$10 μm thick) were held between a conventional glass microscope slide and cover slip. A Leitz Laborlux 12 Pol microscope equipped with long working distance objectives was used. Microstructures (textures) characteristic of elevated temperatures were observed on a Linkam 26-THM-600S heating/freezing stage equipped with a 26-PR-600 controller. This provided for a variety of heating/cooling rates as well as for viewing under isothermal conditions. It was possible to maintain specimen temperatures to within 0.1°C of any set point.

Differential Scanning Calorimetry (DSC)

Thermal analysis was performed on a Du Pont 1090 system. Specimens with a mass of 7 mg (approx.) were maintained in an atmosphere of dry nitrogen and scanned at 5°C per minute. A typical thermal history consisted of the following sequence: as-synthesized material was heated to approximately 10°C above the temperature at which it becomes optically isotropic. The specimen was then cooled to room temperature at the same rate, and the heating cycle was then repeated immediately.

RESULTS AND DISCUSSION

All three compounds are crystalline solids at room temperature. Table I lists transitions observed by light microscopy, for both heating and cooling. The liquid crystalline phase formed on heating is identified as smectic B on the basis of its distinctive mosaic texture (Figure 1a). Because the texture contains some domains that are homeotropic, and some that are equiaxed, tilted smectics are eliminated from consideration.[1] In all cases, the smectic B phase is stable over only a very narrow temperature range (0.4°C or less) on heating. The smectic B-isotropic

TABLE I

Transitions detected by light microscopy. Heating/cooling rate through well-defined transitions is 0.1°C/min.

Compound	Heat/cool	Transitions
F10H10F10	Heat	crystalline solid → 111.5°C → smectic → 111.8°C → isotropic
	Cool	isotropic → 111.8°C → smectic → variable → crystalline solid
F12H8F12	Heat	crystalline solid → 137.2°C → smectic → 137.6°C → isotropic
	Cool	isotropic → 137.6°C → smectic → variable → crystalline solid
F12H12F12	Heat	crystalline solid → 136.4°C → smectic → 136.7°C → isotropic
	Cool	isotropic → 136.7°C → smectic → variable → crystalline solid

transition is reversible, i.e. the transition temperature is the same for heating and cooling.

On further cooling below this temperature, the mosaic texture eventually undergoes a transformation to a very much finer microstructure (Figure 1b, c). The new microstructure consists of narrow, elongated domains that appear to have a well-defined orientation relative to the edges of the parent smectic B domains. This orientation relationship indicates that the molecules must develop a tilt relative to the smectic layer normal, as crystallization proceeds.[1] The transformation to the fine microstructure does not take place instantaneously at a well defined temperature. Depending on the extent to which the sample is supercooled, the transformation is seen to occur over a period ranging from several minutes to several hours, and there is some uncertainty as to when the transformation is complete. In this respect, the tri-block materials behave similarly to the di-block compounds F10Hn. The sluggishness of the transition between ordered phases in F10Hn was attributed[1-2] to the kinetic barrier associated with the accompanying relative longitudinal displacement of adjacent molecules. Indeed, we expect the kinetics to be even more sluggish in the tri-block materials, because of the higher molecular weight. Also, the supercooling associated with formation of the low temperature ordered phase is greater in the tri-block compounds, consistent with this phase being crystalline.

Neither DSC in the present study, nor use of the Raman-active longitudinal acoustical mode (LAM) in previous studies,[6] indicates the presence of the smectic B phase in the tri-block compounds. The crystal → smectic B and smectic B → isotropic transitions lie too close together to yield separate DSC endotherms on

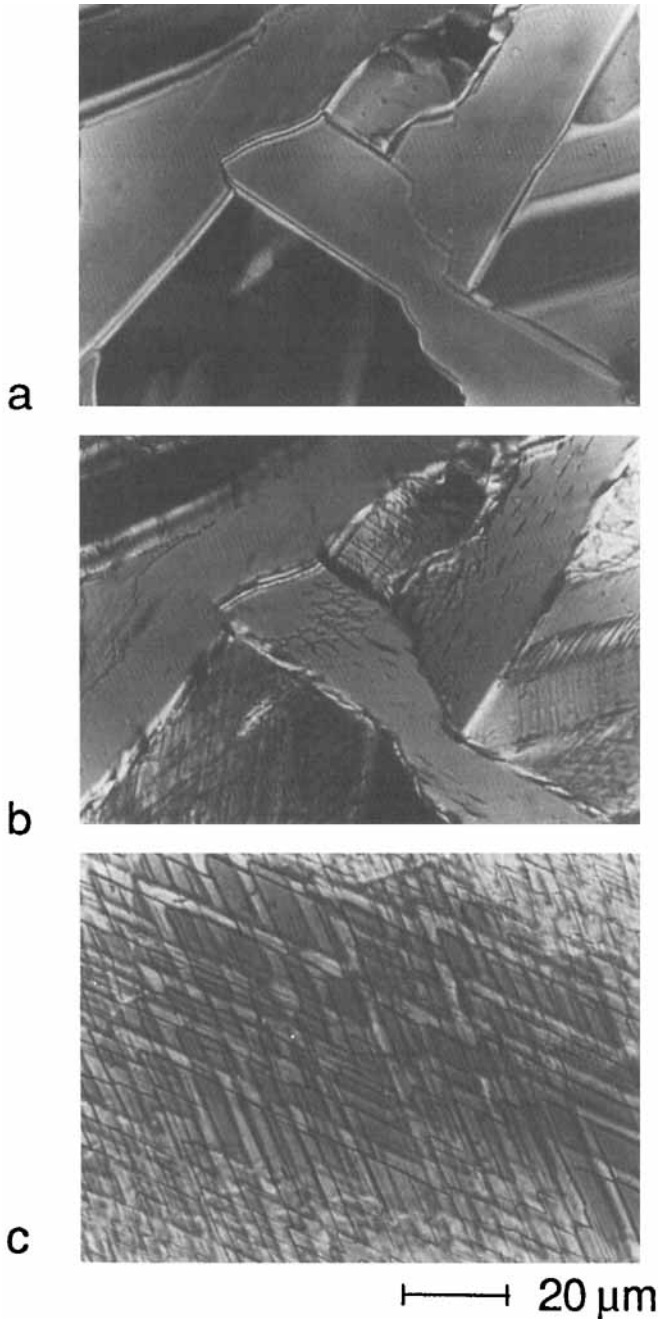

FIGURE 1 Microstructures of F12H8F12, observed between crossed polars in the transmitted polarized light microscope. a) Mosaic texture at 137.3°C after cooling the sample at 0.1°C from the isotropic melt. b) The same field of view, after further cooling at 10°C/minute to 65°C. The ingrowth of crystalline material is evident. c) Another view of the same sample, showing the interior of a large smectic domain after crystallization has been allowed to proceed for a further 30 minutes at 65°C.

heating. However, the narrow stability range of the smectic B phase on heating may account for the previously noted[6] breadth of the single DSC endotherm. In experiments using the LAM,[6] sample temperatures were measured with an uncertainty of $\pm 3°C$, so it is unlikely that a phase with a maximum equilibrium stability range of 0.4°C could be detected by using this technique. On cooling, the transition between smectic B and crystal proceeds so slowly that the accompanying latent heat is released over a wide range of temperature and time, and is therefore not detected in the DSC data.

CONCLUSIONS

1. While the tri-block semifluorinated compounds F10H10F10, F12H8F12 and F12H12F12 lack the rigid mesogenic groups typical of liquid crystals, there is a narrow temperature range over which they form a stable smectic B phase.
2. The transition between the smectic B and crystalline phases is sluggish on cooling, indicating a significant barrier to the relative longitudinal displacement of adjacent molecules.
3. The existence of a well-defined orientation relation between crystalline material and the parent smectic B domains indicates that the molecules become tilted away from the smectic layer normal as crystallization proceeds.
4. The smectic-isotropic transition temperature is sensitive to the length of the fluorinated blocks, and relatively insensitive to the length of the alkane segment (Table 1).

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