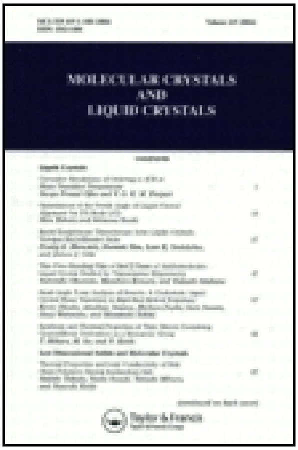

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Structures of the liquid crystalline phases formed in the mesogens with perfluorinated substituents

Etsushi Nishikawa [a] , Jun Yamamoto [a] & Hiroshi Yokoyama [a b]

[a] Yokoyama Nano-structured Liquid Crystal Project, ERATO, Japan Science and Technology Corporation, Ibaraki, Tsukuba, Japan

[b] Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Ibaraki, Tsukuba, Japan

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STRUCTURES OF THE LIQUID CRYSTALLINE PHASES FORMED IN THE MESOGENS WITH PERFLUORINATED SUBSTITUENTS

Etsushi Nishikawa, Jun Yamamoto
Yokoyama Nano-structured Liquid Crystal Project, ERATO,
Japan Science and Technology Corporation, 5-9-9 Tokodai,
Tsukuba, Ibaraki 300-2635, Japan

Hiroshi Yokoyama
Yokoyama Nano-structured Liquid Crystal Project, ERATO,
Japan Science and Technology Corporation, 5-9-9 Tokodai,
Tsukuba, Ibaraki 300-2635, Japan
Nanotechnology Research Institute, National Institute of Advanced
Industrial Science and Technology ,1-1-4 Umezono, Tsukuba,
Ibaraki 305-8568, Japan

Liquid crystalline behavior and microstructures of the mesogens with a perfluorinated substituent and a site for forming hydrogen bonding (-COOH or -OH) were investigated, in which two important non-covalent (fluorophilic/fluorophobic, hydrogen bonding) interactions can work.

All of the compounds under investigation form two smectic phases, a smectic C phase and a smectic A phase. The phase transition between the two phases was observed with DSC, showing different amounts of enthalpy changes. One of the compounds showed a latent heat of $5.3\,kJ \cdot mol^{-1}$*, indicating that the smectic A to smectic C phase transition is probably of first order, while on another one an enthalpy change of* $0.13\,kJ \cdot mol^{-1}$ *was measured. With temperature depending X-ray experiments on the compound showing a large latent heat an abrupt tilt angle change at the phase transition was measured, which revealed the first order phase transition feature. The frustration of microsegregation structures of the studied compounds could be one of the origins to the first order smectic A to smectic C phase transition.*

Keywords: hydrogen bonding; microsegregation; perfluoroalkyl chains; phase transition; smectic phase

Address correspondence to Etsushi Nishikawa, Yokoyama Nano-structured Liquid Crystal Project, ERATO, Japan Science and Technology Corporation, 5-9-9 Tokodai, Tsukuba, Ibaraki 300-2635, Japan.

INTRODUCTION

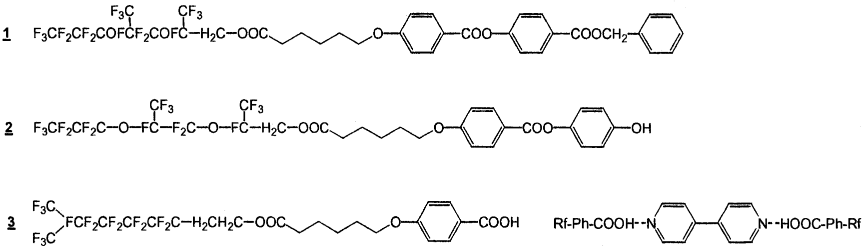
Recently low molecular and macromolecular mesogens with perfluorinated substituents have been intensively investigated, which can form liquid crystalline phases e.g. smectic phases and columnar phases with intriguing microsegregation structures [1]. In the last decade hydrogen bonding interaction has been recognized as an effective pathway to self-organization to variety of liquid crystalline structures [2].

In this report we have studied mesogens with a perfluorinated chain and a hydrogen bonding active site, thus exhibiting both fluorophilic/fluorophobic and hydrogen bonding interactions. It has been found that the materials under investigation form two liquid crystalline lamellar phases, a smectic A phase and a smectic C phase. We discuss the smectic A to smectic C phase transition of these compounds by means of differential scanning calorimetry and X-ray diffraction technique. Due to the frustration of microsegregation structures the first order smectic A to smectic C phase transition occurs.

EXPERIMENTAL

Chemical structures of the compounds under investigation **1**–**3** are shown in Scheme 1. The syntheses of these materials will be described elsewhere. The compound **1** has no hydrogen bonding active site, while **2** has a –OH group. The material **3** is a hydrogen bonded complex between the benzoic acid derivative and 4,4′-dipyridyl. **1** and **2** have a bulky fluorinated moiety, while **3** has an end-branched perfluoroalkyl substituent.

Differential scanning calorimetry (DSC) data were recorded with a MAC Science DSC-3100 at a heating/cooling rate of 2 k/min. X-ray diffraction (XRD) measurements were carried out with monochromatic CuK_α radiation ($\lambda = 1.54\,\text{Å}$) using an X-ray machine with a two-dimensional detector.



SCHEME 1 The chemical structure of investigated materials.

RESULTS AND DISCUSSION

In Table 1 phase transition temperatures of the studied materials are summarized together with enthalpy changes. All the compounds **1**–**3** show a smectic A to smectic C phase transition with the corresponding enthalpy changes of 0.13, 1.6 and 5.3 $\mathrm{kJ{\cdot}mol^{-1}}$, respectively. The latent heat of **3** is large, indicating that the phase transition is possibly of first order, whilst that of **1** is small. The enthalpy change of **2** is relatively large, indicating that the smectic A to smectic C phase transition could be also of first order. Note that the enthalpy change of the smectic A to isotropic phase transition of **2** is remarkably small (0.7 $\mathrm{kJ{\cdot}mol^{-1}}$).

In order to ascertain the phase transition behaviour, temperature depending XRD experiments are carried out. In case that smectic A to smectic C phase transition is of first order, the tilt angle emerges abruptly at the phase transition temperature. If the transition is of second order, the tilt angle changes gradually and continuously. Figure 1 shows the results, measured in the compound **3**, the hydrogen bonded complex. Figure 1a shows the original intensity profiles at small angles around the phase transition temperature. The data exhibited in Figure 1b–1d are calculated from the original data of Figure 1a.

Figure 1b shows that the d-spacing and the tilt angle abruptly change at the smectic A to smectic C phase transition temperature. The intensity and the half value width also change discontinuously at the phase transition, as seen in Figure 1c and 1d, respectively. These results, the steep tilt angle change together with the described discontinuous changes of the physical values measured with XRD and the large enthalpy change can assert that the smectic A to smectic C phase transition of the material **3** is of first order.

Figure 2 summarizes the tilt angle changes of the compounds **1**–**3**. In contrast to **3**, the compound **1** shows a moderate tilt angle change, indicating that the smectic A to smectic C phase transition is of second order. The behaviour of the smectic A to smectic C phase transition of **2** seems similar to that of **3**.

TABLE 1 Phase Transition Temperatures (°C) and Corresponding Enthalpy Changes [$\mathrm{kJ{\cdot}mol^{-1}}$] of the Materials Under Investigation Determined with DSC in the Heating Process at the Scanning Rate of 2 K/min

	Cr	S_C	S_A	I
1	● 52 [39]	● 59 [0.13]	● 84 [3.4]	●
2	● 61 [9.3]	● 88 [1.6]	● 96 [0.7]	●
3	● 106 [39]	● 157 [5.3]	● 161 [13]	●

Cr = crystalline; S_C = smetic *C*; S_A = smetic *A*; I = isotropic.

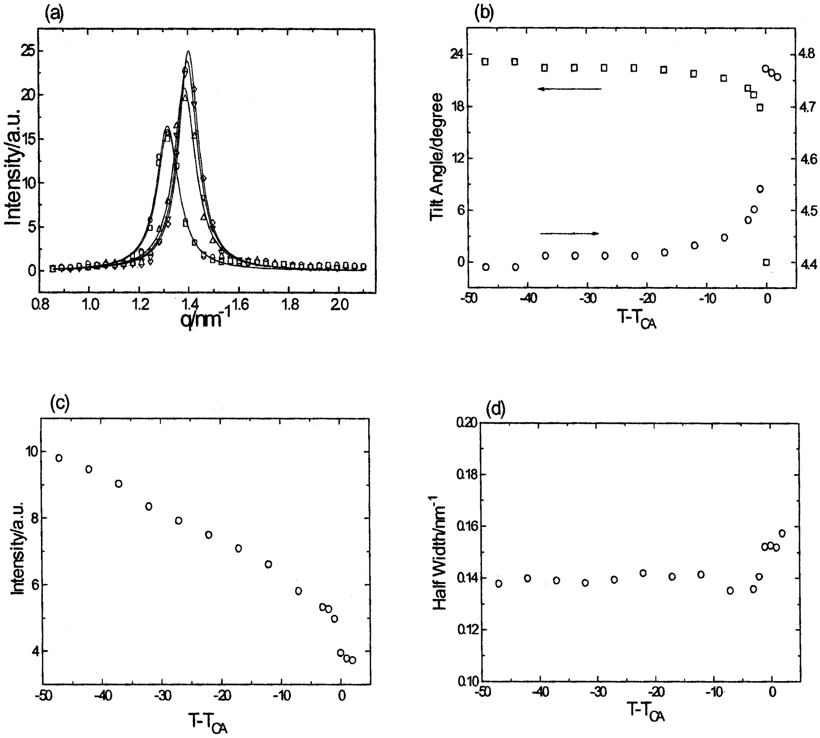


FIGURE 1 (a) Original Intensity profiles at small angles observed in 3 at (□) 159°C, (○) 158°C, (△) 157°C, (▽) 156°C and (◇) 155°C; (b) (○) temperature dependent d-spacing and (□) tilt angle; (c) temperature depending Intensity; (d) temperature depending half value width, thereby T denotes the measurement temperature and T_{CA} the smectic C to smectic A phase transition temperature of 157°C.

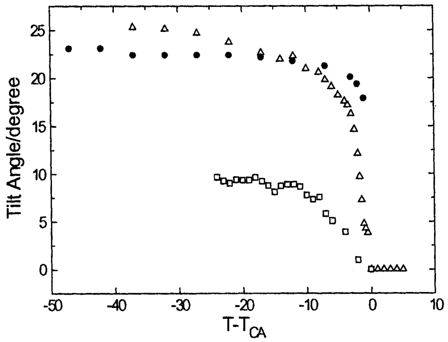


FIGURE 2 Temperature depending tilt angles observed in (□) 1, (△) 2 and (●) 3.

We suppose the reason why the smectic A to smectic C phase transition of **3** occurs of first order as follows. The d-spacing of **3** at the smectic A phase is 4.8 nm, while the molecular contour length calculated with MOPAC is 6.5 nm. Therefore for the structure of the smectic A phase an interdigitation should be considered. If the alkyl chain is interdigitated with the perfluoroalkyl chain, the calculated layer spacing is consistent with the observed d-spacing. In this case, thus, the segregation between the alkyl group and the perfluoroalkyl moiety does not occur yet, resulting in a frustrated structure. With decreasing temperature the incompatibility between these moieties increases not to persist the overlapping (interdigitation) so that the segregation between them occurs [3]. Furthermore a conformational change also could occur leading to a zigzag molecular form [4]. With these changes of frustrated microstructures the smectic A to smectic C phase transition could take place as the first order phase transition.

CONCLUSIONS

Mesogens with a perfluorinated moiety and a hydrogen bonding active site have been synthesized and found to exhibit the first order smectic A to smectic C phase transition that was determined with thermal analysis showing a large latent heat and X-ray diffraction technique observing a steep tilt angle change. The frustration of microsegregation structures of the materials is one of the origins to the phase transition exhibiting first order nature.

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