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# A polycatenar mesogen with a perfluorinated moiety showing continuous phase transformation between a smectic A phase and a structured, fluid, optically isotropic phase

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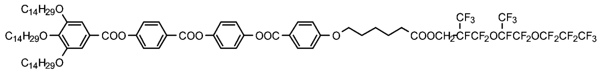
**A polycatenar mesogen consisting of a four aromatic ring system with three long alkoxy chains and a bulky perfluorinated substituent has been synthesized and found to show the polymorphism of a cubic phase, a columnar phase and a smectic A phase, including a structured, fluid, optically isotropic phase with the phase transformation between the smectic A phase and the isotropic phase occurring continuously.**

Liquid crystals composed of hard and soft hydrocarbon moieties bound chemically to construct unique chemical architectures have been intensively investigated in the last two decades. In addition to the conventional rod-like and disc-like mesogens, long-core swallow-tailed,[1] polycatenar,[2] bend-shaped,[3] pyramidal-shaped[4] compounds *etc.* have been synthesized and their liquid crystalline phase behaviour and physical properties studied. Due to the characteristic molecular shapes and the difference in the rigidity of stiff and flexible segments in these materials, *i.e.* incompatibility between the segments from the structural point of view, molecular packing importantly rules the organization of liquid crystalline phases.[5] Amphiphilic mesogens consisting of two chemically immiscible segments covalently combined have been recently attracting much attention due to the possibility to form a variety of liquid crystalline phases with fascinating microstructures.[6] For instance, materials composed of hydrocarbon core segments with polyol moieties,[7] siloxane parts,[8] or perfluorinated chains[9] *etc.* have been investigated, which exhibit high incompatibility among the constitutional moieties, and are found to form intriguing micro-separated/nano-segregated structures. It is recognized that incompatibility among molecular segments from both the chemical and geometrical points of view is crucial in order to develop liquid crystalline compounds self-organizing into remarkable microstructures.

In this paper we investigate a polycatenar compound of unique molecular architecture as shown in Scheme 1, consisting of a stiff planar four-ring aromatic core with three bulky, flexible tetradecyloxy chains attached on one terminal ring and a perfluorinated substituent on the other end. In this system, the long alkoxy chains are incompatible with the aromatic core from the structural point of view while the perfluorinated moiety is incompatible with the remaining hydrocarbon parts mainly from the chemical point of view, thus two important aspects concerning incompatibility are combined.

The detailed synthesis of this polycatenar compound will be reported elsewhere. The chemical structure was assigned by using elemental analysis, mass spectrometry and $^1$H NMR spectrometry. The phase behaviour of the material was determined with differential scanning calorimetry (DSC), polarized optical microscopy (POM) and X-ray diffraction (XRD). On heating, the crystalline phase transforms into a cubic phase at 52.6 °C, which is recognized by observing the entire field under POM becoming extinct, exhibiting no birefringence that is characteristic to cubic phases.[10] Then a columnar phase appears at 65.3 °C, which transforms to a smectic A phase at 94.2 °C, followed by an isotropic phase transformation at 116 °C. On cooling , the isotropic to smectic A phase transformation occurs at 115 °C. In the smectic A phase almost perfect planar molecular alignment parallel to the rubbing direction is observed between polyimide-coated glass plates, while homeotropic alignment is observed between non-coated glass plates. Then the columnar phase appears at 94 °C, where a characteristic focal-conic texture is observed between normal glass plates as shown in Fig. 1(a). Between polyimide-coated glass plates the columnar phase exhibits a structure as demonstrated in Fig. 1(b). The columnar phase transforms to a dark (small birefringent regions still exist) liquid crystalline phase at 59 °C, which should be the cubic phase. Then crystallization takes place at 40.3 °C.



**Scheme 1** Chemical structure of the polycatenar compound.

Therefore the polycatenar compound exhibits liquid crystalline polymorphism in the phase sequence of a cubic phase, a columnar phase and a smectic A phase. The phase transition temperatures are summarized as follows.

$$\mathrm{Cr} \xrightleftharpoons[52.6]{40.3} \mathrm{Cub} \xrightleftharpoons[65.3]{59} \mathrm{Col} \xrightleftharpoons[94.2]{94} \mathrm{SmA} \xrightleftharpoons[116]{115} \mathrm{Iso}$$

Fig. 2 shows a DSC chart obtained at a heating/cooling rate of 2 K min$^{-1}$. The phase transition between the columnar phase and the smectic A phase is detected as a very weak peak at about 94 °C with an enthalpy change of 0.07 kJ mol$^{-1}$. The smectic A to isotropic phase transformation is observed around 115 °C as a small peak with an enthalpy change of 0.34 kJ mol$^{-1}$, which is considerably smaller compared to conventional latent heat values for smectic A to isotropic phase transformations of around 5–10 kJ mol$^{-1}$.[11] This remarkable result indicates that the smectic A to isotropic phase transformation of this material takes place in a unique fashion.

With POM in the smectic A phase, either homeotropic or planar molecular alignment was observed as described already.

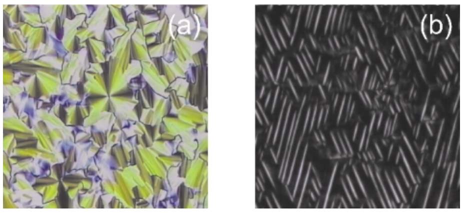


**Fig. 1** Polarized optical photomicrographs observed in the columnar phase of the polycatenar compound (a) between normal glass plates at 90 °C, showing a focal-conic texture and (b) between polyimide-coated glass plates at 75 °C, showing a characteristic structure.

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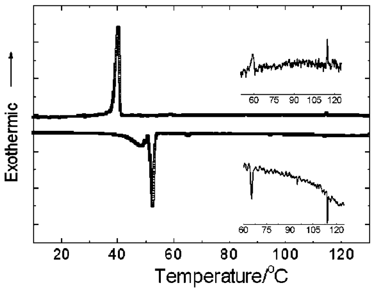

**Fig. 2** DSC chart measured at a heating/cooling rate of 2 K min$^{-1}$. The region from 55 to 125 °C is magnified and shown in the inserts.

In both cases we have, as yet, not observed bâtonnet formation. Bâtonnets normally grow at isotropic to smectic A phase transformations on cooling, where the two phases coexist as a consequence of a first order phase transformation.[12] The absence of bâtonnet formation indicates that the isotropic to smectic A phase transformation of the material is probably of second order.

We performed temperature dependent XRD experiments in order to study the unique isotropic (Iso) to smectic A phase transformation. In the smectic A phase a sharp small-angle reflection resulting from lamellar structure is observed, which reveals a $d$-spacing of 8.3 nm at 114 °C. As the molecular length with the all-*trans* conformation of the alkyl chains is calculated to 6.0 nm, an interdigitated bilayer structure of the smectic A phase is probable.

Fig. 3 shows the original intensity profiles at small angles observed at various temperatures in the range from 140 to 112 °C. A small-angle reflection is clearly observed at high temperatures far above the smectic A to Iso phase transformation temperature. This fact indicates that the Iso phase is not a normal isotropic liquid phase but rather a structured, fluid, optically isotropic liquid. Fig. 4(a), shows the temperature dependent $d$-spacing, which was calculated from the original XRD data. The $d$-spacing decreases with increasing temperature in the smectic A phase. Then without a discontinuous jump at the smectic A to Iso phase transformation temperature of 115 °C, the $d$-spacing continuously decreases with increasing temperature further and more steeply in the Iso phase. Moreover we have observed that the half width of the small angle reflection also changes continuously as shown in Fig. 4(b). These results of the X-ray experiments reveal that the smectic A to Iso phase transformation of the polycatenar compound is continuous. It is also unique.

As mentioned above, the Iso phase is fluid and optically isotropic like normal liquids, but structured remarkably. Owing to the significant feature of the material, *i.e.* the extremely high incompatibility among the constitutional moieties, microseparation can still exist even after the long-range orientational order and quasi long-range positional order of the lamellar structure of the smectic A phase are removed, resulting in the Iso phase. Nevertheless it is very interesting that the smectic A to Iso phase transformation occurs continuously and this kind of phase transition phenomena has never been observed before. We are now synthesizing related polycatenar compounds and investigating the remarkable phase transformation between the smectic A phase and the Iso phase in detail.

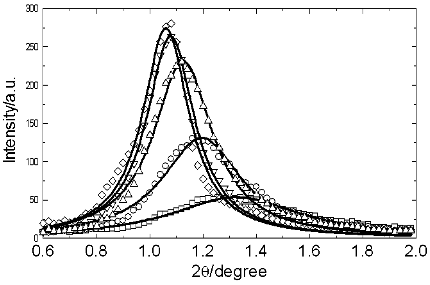

**Fig. 3** Intensity profiles at various temperatures of (□) 140 °C, (○) 130 °C, (△) 124 °C, (▽) 118 °C and (◇) 112 °C.

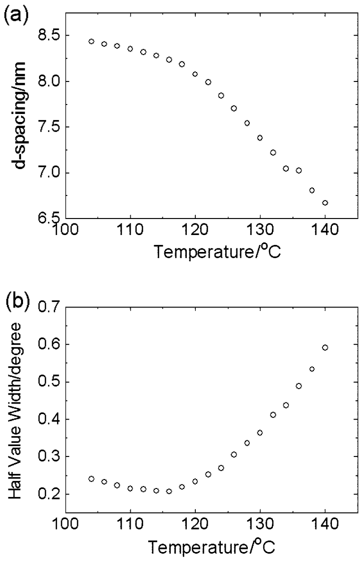

**Fig. 4** (a) Temperature dependent $d$-spacing obtained from the small-angle reflection. (b) Temperature dependent half width of the small-angle reflection.

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