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New Liquid Crystalline Phases with Layerlike Organization

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Received July 26, 2002

The investigation of the driving forces behind molecular self organization is one of the most exciting research areas. Thereby, liquid crystalline phases are of special interest, because they combine order and mobility on a molecular, supramolecular, and macroscopic level. Most mesophases of conventional rodlike or disklike LC materials[1] are quite simple, but exciting new mesophase morphologies have recently been realized with rodlike bolaamphiphiles **1** carrying a long lateral alkyl chain.[2] Such molecules represent ternary block molecules in which three incompatible blocks (polar diol groups, rigid aromatic cores, and flexible lipophilic chains) are combined in a competitive and nonlinear manner. As a consequence, each of these units segregates into its own subspace, leading to a series of unusual columnar mesophases. They are built up by columns which are filled by the microsegregated fluid alkyl chains. These columns are separated by the rigid biphenyl cores which are held together at their ends and side-by-side by hydrogen-bonding networks, thus forming walls around these columns.[2] Figure 1 shows, as an example, the honeycomblike structure, suggested for the hexagonal columnar mesophase (Col_h) of compound **1**. The question arose, what may happen if the space required by the nonpolar lateral chains is further increased, so that formation of cylinders becomes unfavorable.

Herein we report novel mesophases obtained with the new mesogenic block molecule **2**, in which the lateral alkyl chain is replaced by a semiperfluorinated chain.[3] This chain requires much more space than related hydrocarbon chains, which dramatically changes the self organization.[4] This compound was investigated by differential scanning calorimetry (DSC), polarized light optical microscopy (PM), and X-ray diffraction of aligned samples. Three distinct mesophases can be detected by PM on cooling from the isotropic liquid state (see Figure 2). The high-temperature mesophase, occurring between 195 °C (clearing transition: $\Delta H = 1.1$ kJ/mol) and 166 °C, behaves like a conventional SmA phase, characterized by a typical fanlike texture (Figure 2a) which can easily be aligned homeotropically, appearing completely dark between crossed polarizers (Figure 2b). On cooling, at 166 °C a fluid schlieren texture appears (Figure 2e) which indicates the transition to an optically biaxial mesophase. A characteristic feature of this schlieren texture is the absence of four-brush-disclinations. This excludes an SmC-like organization in which the molecules are tilted with respect to the layer planes, which is often found in conventional LC materials below SmA phases. In the regions with fan-shaped texture (Figure 2a) a strong change of the birefringence can be observed at the phase transition, whereby the color changes from yellow via red, violet, blue, green to yellow again, but the fans do not become broken or change their shape (Figure 2d). These textural features have been predicted for biaxial SmA phases (SmA_b, McMillan phase)[5] and recently have been observed experimentally for such a mesophase.[6] The transition to a third mesophase at 165 °C (enthalpies of the transitions at 165 and 166 °C cannot be resolved or one of them is of second order, $\Sigma\Delta H = 2.6$ kJ/mol) can be seen by the transition of the schlieren texture into a paramorphotic mosaiclike texture (Figure 2h), whereby in the regions with fanlike texture only the color slightly changes from deep yellow to red (Figure 2g). This supposes that the layer structure itself remains nearly unchanged in all three phases, whereas the order within the layers dramatically changes.

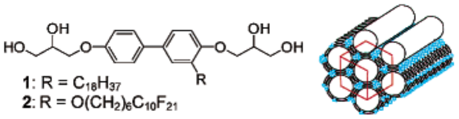

Figure 1. Molecular structures of compounds **1** (phase transitions T/°C: Cr 59 Col_h 141 Iso)[2] and **2** (Cr 135 Lam_A 165 SmA_b 166 SmA 195 Iso) and organization of the molecules of compound **1** in the hexagonal columnar mesophase (Col_h; blue = hydrogen-bonding networks of the terminal diol groups; white = cylinders containing the lateral alkyl chains; gray = aromatic biphenyl cores). The organization of compound **2** is shown in Figure 2. Other abbreviations: Cr = crystalline, Iso = isotropic liquid.

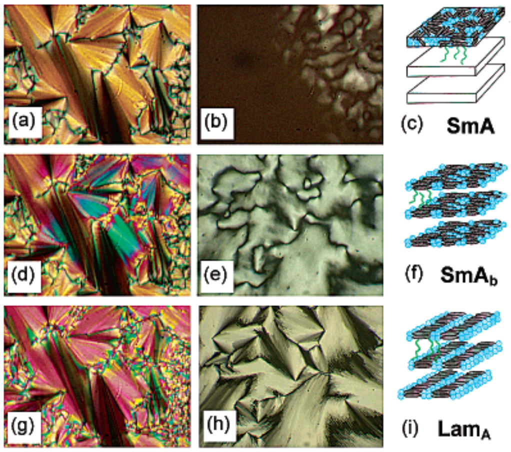

Figure 2. Textures (crossed polarizers) of the mesophases of compound **2**: (a), (b) at 166.5 °C, in the upper right corner of (b) the transition to the biaxial smectic phase can already be seen; (d), (e) at 165.5 °C; (g), (h) at 150 °C; and (c), (f), (i) models of the organization of **2** in the distinct mesophases.

The X-ray diffraction pattern in all three mesophases are characterized by a diffuse scattering in the wide-angle region, which indicates the fluid state of this mesophase. Additionally, in the small-angle region there are four sharp equidistant reflections indicating the presence of a well-defined layer structure. The layer thickness is 3.94 nm at $T = 127$ °C and is temperature-independent ($d = 3.94$ nm at 187 °C), that is, it does not change at the transitions

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10.1021/ja027869x CCC: $22.00

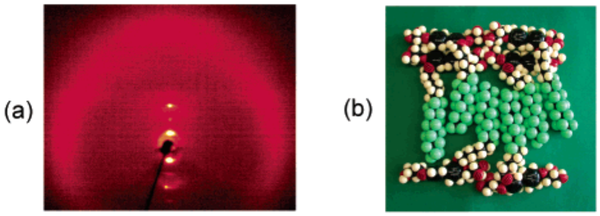

Figure 3. (a) X-ray diffraction pattern of an aligned sample of **2** at 127 °C (supercooled state of the $\mathrm{Lam_A}$ phase) and (b) model showing the organization of the molecules in the smectic phases.

to the other mesophases. Also the other features of the diffraction pattern do not change at the phase transitions. Another important feature of the X-ray diffraction pattern of an aligned sample, shown in Figure 3a, is that the diffuse wide angle scattering forms a noncircular ring with maxima corresponding to $D = 0.52$ nm in the equator and to $D = 0.46$ nm in the meridian. This diffraction pattern is completely different from conventional fluid smectic phases which show crescentlike halos.

The PM observations in connection with the peculiarities of the X-ray pattern lead to the models of the mesophase structures, shown in Figures 2c,f,i and 3b. Accordingly, the layer structure itself should be the result of the segregation of the nonpolar lateral chains from the bolaamphiphilic cores (biphenyl units and terminal diol groups), but in contrast to all conventional smectic phases, the calamitic biphenyl cores are organized *parallel to the layer planes*. The aromatic layers are separated by the nonpolar layers of the lateral chains which are strongly disordered (liquidlike) but with a certain preferred direction of the fluorinated segments perpendicular to the layer planes ($D = 0.52$ nm is close to the value for the mean distance between perfluorinated chains corresponding to $D = 0.54$ nm). The experimentally determined layer distance requires that the thickness of the aromatic sublayers should correspond to in average about three parallel aligned biphenyl cores. In this case the thickness of the hydrocarbon sublayers (aromatic cores + alkyl segments of the lateral chains) is approximately the same as the thickness of the perfluorinated sublayers, which explains the weak 02-reflection in the diffraction pattern. According to X-ray scattering and optical investigations the layer structure is maintained in all three mesophases. Therefore, the phase transitions should be due to a reorganization of the biphenyl cores within the aromatic sublayers which led us to propose the following models for the mesophases.

The high-temperature mesophase (SmA) is an optically uniaxial mesophase with a fluid layer structure. In this phase the biphenyl cores should be aligned in average parallel to the layer planes and there is no long-range order between the cores within the layers (see Figure 2c).[7,8] The mesophase below this SmA phase, which has only a very small existence region, is an optically biaxial smectic A phase ($\mathrm{SmA_b}$, see Figure 2f). Here, the biphenyl cores should adapt a long-range orientational order within the aromatic sublayers, and the individual layers are orientationally correlated with each other, so that optical biaxiality of the bulk sample results. This phase can be regarded as a smectic phase built up by quasi 2D layers with nematic order, separated by isotropic layers of the lateral chains. The transition from the $\mathrm{SmA_b}$ phase to the low-temperature phase is characterized by the reduction of the fluidity in the layers as indicated by the transition from a schlieren texture to a mosaiclike texture. This means that additional order should occur at this phase transition. In analogy to the phase sequence Iso-N-SmA, which is often observed in conventional LC systems by decreasing the temperature, it can be assumed that in the low-temperature mesophase of **2** the bolaamphiphilic cores adapt an additional positional order within the aromatic sublayers. This is due to the segregation of the hydrogen-bonding networks from the aromatic cores, leading to an additional periodicity within these sublayers ($\mathrm{Lam_A}$, see Figure 2i). Here, microsegregation occurs on two distinct levels: The segregation of the nonpolar chains from the aromatic cores leads to the "bulk" layer structure and segregation of polar and aromatic subunits within the aromatic sublayers gives rise to an additional periodicity within these sublayers. This phase can be regarded as a smectic phase built up by quasi 2D layers with "SmA-like order" in the layers, separated by isotropic layers of the lateral chains. (Figure 2i). However the additional repeat distance within the aromatic sublayers—which is expected to occur perpendicular to the layer reflection at the equator of the two-dimensional X-ray diffraction pattern—cannot be found. This could be explained, if it is assumed that the electron density modulation within the 2D smectic sublayers is low.[9] Then, the intensity of the corresponding reflections is very weak. Additionally, there should be no positional correlation between adjacent layers (no cross reflections), which means that this is a sliding phase.[10]

These results show that the competitive combination of micro-segregation and rigidity is an appropriate way to new exciting mesophase morphologies, which are quite distinct from all known mesophases. The successive enlargement of the lateral chains leads to a transition from conventional smectic phases, in which the molecules are aligned perpendicular to the layer planes (**1**, R = H)[2] to columnar mesophases with network structures (Figure 1)[2] and finally to a completely novel type of smectic phases, where rigid rodlike segments are organized parallel to the layer planes (Figure 2). It could be expected that a diversity of novel mesophases with one-, two-, and three-dimensional long-range order will result from different arrangements within the aromatic layers (tilted or more ordered structures) as well as from positional correlation between the layers.

Acknowledgment. The work was supported by the Deutsche Forschungsgemeinschaft (DFG).

Supporting Information Available: Analytical data of **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA027869X