DOI: 10.1002/cphc.201100739

# Interplay between H-Bonding and Alkyl-Chain Ordering in Self-Assembly of Monodendritic L-Alanine Derivatives

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This paper reports on the synthesis and self-organizing properties of monodendrons consisting of L-alanine at the focal point and alkyl chains with different length at the periphery. The structures of thin films and monolayers are studied by temperature-resolved grazing-incidence X-ray diffraction and scanning force microscopy. The interplay between H-bonding and ordering of the alkyl chains results in a rich temperature-dependent phase behavior. The monodendrons form H-bonded stabilized clusters with the number of molecules depending on the length of the aliphatic chains and temperature. The clusters play the role of constitutive units in the subsequent self-assembly. Short alkyl chains allow the material to form thermodynamically stable crystalline phases. The molecules with longer side groups exhibit additional transitions from the crystalline phase to thermotropic columnar hexagonal or columnar rectangular liquid-crystalline phases. In monolayers deposited on highly ordered pyrolytic graphite, the materials show ordering similar to thin films. However, for the compound bearing hexadecyl chains the affinity of the alkyl groups to graphite dominates the self-assembly and thereby allows epitaxial growth of a 2D lattice with flat-on oriented molecules.

### 1. Introduction

Self-assembly of functional molecular building blocks through noncovalent interactions has attracted considerable interest, not only for fundamental research, but also for possible applications as a bottom-up approach for construction of molecular-scale devices or biologically active materials.<sup>[1-3]</sup> Well-defined architectures can be fabricated by using the principle of molecular recognition exploited by nature. In particular, this approach is convenient for building regular H-bond networks selectively formed between specially designed centers in solution or in the solid state. Self-assembly through H-bonded networks is advantageous due to the thermal reversibility of these bonds, which enables formation of a system prone to undergo repeated formation or breakdown of connectivity. One of the prospective classes of H-bonding molecules capable of self-organization consists of proteinogenic amino acid based amphiphililes, for example, L-alanine derivatives. These chiral organic molecules can self-assemble into a variety of supramolecular architectures such as vesicles,<sup>[4-6]</sup> helical ribbons,<sup>[7]</sup> and ropes, as well as fibrous and tubular structures.<sup>[6]</sup> In addition, FTIR studies on N-octadecanoyl L-alanine monolayers at the air/ water interface indicated that formation of H-bonding networks by the amino acid resulted in enhanced interaction of hydrocarbon chains.<sup>[8]</sup> At the same time, monodendritic mesogens derived from gallic acid were shown to be appropriate building blocks for fabrication of complex thermotropic or lyotropic mesophases of different symmetry.<sup>[9-11]</sup> Gin et al. reported the synthesis of 3,4,5-tris(11'-acryloxyundecyloxy)benzoyl Lalanine, a monodendritic amphiphile which self-assembles into an inverted hexagonal lyotropic liquid-crystalline phase.[12,13]

The majority of the applications of amphiphilic molecules rely on controlled structure formation at interfaces and on surfaces.<sup>[14]</sup> In thin films, the behavior of these molecules differs from that in the bulk, since the self-assembled structure is sensitive to the interfacial energies (i.e. affinity of the polar molecular core and nonpolar periphery with respect to the substrate) and to the geometrical constraints. For discotic and calamitic molecules two- and three-dimensional structure formation on patterned substrates such as polytetrafluoroethylene,<sup>[13,15-17]</sup> highly-oriented pyrolitic graphite (HOPG),<sup>[18-22]</sup> and inorganic salts<sup>[23-25]</sup> was addressed. The orientation and epitaxial growth of the crystalline domains is believed to be determined by commensurate configuration of the conjugated core with the corresponding substrate crystal face. However, the role of alkyl

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Bruker Nano-Surface Inc. (formerly Veeco Metrology Instruments) 112 Robin Hill Road, Santa-Barbara, CA 93110 (USA) side groups in the self-assembly process is probably underestimated. In our previous works, we have shown the effect of side-chain ordering on structure development for bulk samples, thin films, and monolayers.<sup>[26–30]</sup> The tendency of alkanes to form oriented textures on HOPG was shown by temperature-dependent measurements on single crystals and monolayers of polyethylene<sup>[31]</sup> and long alkanes.<sup>[32]</sup> When prepared by solution casting on HOPG, these materials form single crystals with crystalline stems oriented almost normal to the substrate. However, after annealing at high temperature the crystal morphology evolves to ribbons with chains parallel to the substrate. The chains are accommodated along graphite crystallographic directions with epitaxial relation (110)PE//(0001) HOPG.<sup>[31]</sup> The ordering of linear alkyl chains can thus play an essential role in self-assembly of monodendrons at surfaces.<sup>[33]</sup>

Herein we report on the synthesis and self-assembling behavior of a novel family of monodendrons, namely, *N*-[3,4,5tris(alkyloxy)benzoyl] L-alanine bearing alkyl chains of different lengths (Scheme 1). The effect of the chain length on the structural evolution in the bulk and in thin films was studied by differential scanning calorimetry (DSC) and X-ray grazing-incidence diffraction (GID), respectively. In addition, thin-film morphology and molecular alignment in monolayers on the HOPG substrate were addressed by scanning force microscopy (SFM).



**Scheme 1.** Chemical structure of wedge-shaped *N*-[3,4,5-tris-(alkyloxy)]benzoyl L-alanine bearing alkyl chains of different length **3a–c** on the periphery and *N*-benzoyl alanine **M** at the focal point.

### 2. Results and Discussion

#### 2.1. Synthesis

The monodendrons were synthesized from commercially available L-alanine methyl ester hydrochloride and gallic acid ethyl ester. A simple synthetic route to target monodendrons 3a-c was developed (Scheme 2). 3,4,5-trialkyloxybenzoyl chlorides 1a-c were treated with L-alanine methyl ester hydrochloride in chloroform in the presence of triethylamine as base.<sup>[34]</sup> After stirring at room temperature overnight, the reaction was complete and subsequent washing with water led to the pure



Scheme 2. Synthetic route for the preparation of *N*-[3,4,5-tris-(alkyloxy)]benzoyl L-alanine derivatives **3 a–c**. Conditions: i) HCI-AlaOMe, NEt<sub>3</sub>, CHCl<sub>3</sub>, 0 °C $\rightarrow$ RT, overnight; ii) KOH, EtOH, H<sub>2</sub>O, reflux for 12 h then HCI (conc.)

ester amides **2a–c**, which were directly subjected to the hydrolysis reaction. After acidification of the reaction mixture, **3b** and **3c** crystallized from the reaction mixture in high purity and were directly used for further characterization without additional purification, while **3a** was recrystallized from ethyl acetate.

#### 2.2. Thermal Analysis and X-ray Diffraction Studies on 3a-c

The influence of the alkyl chain length on the thermal transitions and resulting supramolecular self-assembly was investigated by means of DSC and variable-temperature GID. The DSC heating ramps of compound **3a** shown in Figure 1 (top) exhibit one endothermic peak with a maximum at 131.2 °C. The transition was found to be reversible; it occurs at a large supercooling (62.1 °C), which is typical of crystalline materials formed by H-bonding. This conclusion was further confirmed by variable-temperature polarized optical microscopy (POM) measurements, which revealed formation of spherulitic structure characteristic of crystalline materials (Figure 1, bottom).

Figure 2 (left) displays a typical GID pattern of **3a** recorded at room temperature. The observed peaks can be indexed as *hk*0 reflections. The *d* spacings and angular positions of the reflections allow the *a* and *b* parameters of the unit cell, as well as the crystallographic angle  $\gamma$ , to be determined. Other parameters cannot be identified directly due to the absence of mixed *hkl* peaks. However, from the position of the 002 peak on the equator of the pattern at -4.85 Å (not shown here), the projection of the *c* parameter on the {001} direction was computed to be  $c_1 = 9.7$  Å. Based on density considerations, it was concluded that the unit cell of **3a** contains eight molecules organized in four dimers connected by hydrogen bonds

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**Figure 1.** DSC curves of **3 a** recorded during a cooling/heating cycle with dT/dt = 10.0 °C min<sup>-1</sup> (top). The POM image (bottom) shows the presence of spherulites at 85 °C, which developed during crystallization from the melt.



**Figure 2.** GID pattern of **3 a** recorded at room temperature revealing orthorhombic symmetry of the unit cell (left). Schematics showing the structure of the unit cell of **3 a** containing eight molecules organized in four Hbonded dimers (right). The molecules with the heads directed upward are darker and those with the downward orientation are lighter.

(Figure 2, right). Taking into account the observed extinction rules such as h+k=2n for hk0 and h=2n, k=2n, l=2n for h00, 0k0, and 00l, respectively, as well as possible molecular packing of dimers on the lattice, only P21/c symmetry can be retained. Hence, a pseudo-orthorhombic crystal for 3a with  $P2_1/c$  symmetry was selected with the following lattice parameters: a = 39.1, b = 16.4, c = 9.7 Å,  $\alpha = \beta = \gamma = 90^{\circ}$  (cf. Figure 2, left). Every second molecular layer parallel to the ab plane is shifted by a half-period in the *a* direction. It is noteworthy that the molecules in the dimer are not planar, because of different orientations of alanine heads with respect to the plane of the alkyl chains, similar to the conformation found for the crystal structure of 3,4,5-tridodecyloxycinnamic acid.[28] In thin films, the hexyl side chains are oriented normal to the substrate, that is, in the *a* direction, as shown in Figure 2 (right). No structural changes were detected during heating of the film to the melting point at about 110 °C. Importantly, N-benzoyl alanine without side groups forms a crystal structure built of dimers stabilized by H-bonds.<sup>[35]</sup> Therefore, it is likely that for **3 a** the crystal symmetry is mainly determined by aggregation of the alanine cores.

Upon increasing the alkyl chain length the thermal behavior and morphology of the sample change. The first DSC heating ramp shows two transitions with almost equal enthalpy changes (Figure 3, left). The order–order transition at low temperature is attributed to the aliphatic moieties, and the order–



**Figure 3.** DSC curves measured for **3 b** during a cooling/heating/cycle (left). The first heating ramp  $(dT/dt=1.0^{\circ}\text{C min}^{-1})$  is shown by a dotted line, and the first cooling and second heating  $(dT/dt=10.0^{\circ}\text{C min}^{-1})$  ramps are shown as solid lines. The optical micrographs (right) show liquid-crystalline textures of the compound formed during cooling from the isotropic state to 90 and to 50 °C.

disorder transition likely corresponds to dissociation of the Hbonded phase. A significant decrease of the first-peak intensity during the second heating ramp indicates that annealing at room temperature leads to modification of the film morphology. This issue is discussed in more detail below. The PO micrographs recorded at different temperatures reveal fanlike textures typical of liquid-crystalline (LC) ordering (Figure 3, right). A slight change in the birefringence of the material can probably be accounted for by a local rearrangement of the LC phase at high temperatures. The structural evolution of thin films at high temperatures was monitored by GID measurements.

Figure 4 (left) displays the GID patterns of 3b annealed for several days at room temperature. The patterns were recorded at room temperature and at 60 °C. Below about 53 °C the dif-



**Figure 4.** GID patterns of **3 b** (left) recorded at room temperature and at 60 °C. Schematic of the *ab* projection of the unit cell of **3 b** stable at elevated temperatures (right). The Col<sub>h</sub> structure is composed of disklike supramolecular hexamers.

fraction pattern reveals a "smectic-like" phase characterized by an interlayer spacing of 43.0 Å. This distance is comparable to the length of the molecular dimer. In thin films, the layers are parallel to the substrate, similar to sample **3a**. However, at  $60^{\circ}$ C (i.e. above the first endothermic peak) additional offmeridional reflections appear on the pattern (Figure 4, bottom left). The high-temperature modification was identified as a hexagonal columnar phase Col<sub>h</sub>. It is noteworthy that the lattice parameter of the Col<sub>h</sub> phase (43.6 Å) is close to that of the smectic phase.

Figure 4 (right) shows a sketch of the Col<sub>h</sub> structure formed at elevated temperatures. The columns presumably consist of disklike clusters, each of which is formed by six molecules stabilized by H-bonds. The columnar axis is parallel to the substrate plane, which is typical of spin-coated films of discotics and main-chain liquid-crystalline polymers forming columnar phases.<sup>[26,27,36,37]</sup> Interestingly, after cooling to room temperature the hexagonal columnar phase is preserved. It is metastable at room temperature and slowly transforms into the smectic structure, and this results in the increase in the enthalpy of the "smectic–columnar" transition found by DSC.

The DSC curve (1st heating) of **3 c** exhibits two endothermic maxima in the region 50–74 °C corresponding to a phase transition and a melting peak at 110 °C (Figure 5). These thermal events are reproducible on cooling. However, the second heating ramp shows multiple exo- and endothermic events that probably indicate the monotropic nature of these liquid-crystalline phases. The low-temperature transitions were assigned to reorganization of the alkyl moieties, whereas the intense melting peak likely corresponds to dissociation of the H-bonded cores.



**Figure 5.** DSC curves of **3 c** recorded during a cooling/heating cycle. The first heating ramp  $(dT/dt = 1.0 \degree \text{Cmin}^{-1})$  is indicated by a dotted line, and the first cooling and second heating ramps  $(dT/dt = 10.0 \degree \text{Cmin}^{-1})$  are indicated by solid lines.

At room temperature the 2D GID pattern of 3c shows a complex appearance (Figure 6, left). The particular shape of the most intense off-meridional peak can be explained by the presence of two reflections with close radial and angular positions. The detailed analysis of the pattern and its comparison with patterns measured on bulk samples allows us to propose for 3c a model of rectangular columnar phase with both *a* and *b* axes inclined with respect to the substrate (Figure 7). The parameters of the rectangular 2D lattice are the following: a =

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Figure 6. GID patterns of 3 c recorded at room temperature (left) and at  $60^{\circ}$ C (right). The dashed arrows show selected reciprocal space vectors.



**Figure 7.** Schematic representation of the *ab* projection of the rectangular unit cell of **3 c** at room temperature. The ellipses indicate the molecules pertinent to one column.

45.5, b = 83.2 Å;  $\gamma = 90^{\circ}$ . The value of the *c* parameter cannot be determined from the GID patterns alone, as angle  $\beta$  is not known. The unit cell of 3c contains two columns with six molecules in each (Figure 7). Analysis of the observed extinction rules reveals the presence of a glide plane parallel to the b axis. Consequently, the molecules in the two columns should be inclined in opposite directions with respect to the *b* axis (cf. Figure 7). Such a complex molecular arrangement leads to specific orientation of the 3c molecules on the silicon substrate. Thus, according to our pattern indexation, in thin films the (120) plane with the corresponding repeat distance of 21.7 Å is parallel to the substrate. In this case, the intense double peak corresponds to 020 and 100 reflections located at angles of 42.4 and  $47.6^{\circ}$  with respect to the film surface (cf. Figure 6, left). In contrast to 3a and 3b, for this texture the 3c molecules have two alternating orientations on the substrate.

Similarly to the thermal behavior of **3b**, compound **3c** shows a polymorphic transition at elevated temperature. Thus, at 60 °C the 2D GID pattern reveals a second polymorph characterized by a monoclinic lattice with a=43.0, b=16.8 Å, and  $\gamma=82.3^{\circ}$  (Figure 6, right). In contrast to the columnar phase, this polymorph contains molecular dimers similar to the structure of **3a** (Figure 2, right). It is noteworthy that at this temperature the meridional *hk*0 peaks exhibit the azimuthal intensity distribution typical of textures with so-called double-axis averaging, which we previously observed in fibers of a C<sub>60</sub>-substituted porphyrin derivative.<sup>[38]</sup> In contrast to the conventional uniaxial textures, the structure with double-axis averaging allows 2D lattice rotation in the smectic layer plane. Consequently, the high-temperature phase of **3c** loses the well-de-

fined orientation of the a and b axes with respect to the substrate. Moreover, at elevated temperature the misorientation of the layers is probably caused by the onset of film dewetting, which was detected optically. After cooling to room temperature the film structure does not show any further evolution.

Table 1 summarizes the studied molecular structures, including the phase transition temperatures  $T_{\rm tr}$  and enthalpy changes  $\Delta H_{\rm tr}$ . The X-ray diffraction data measured on bulk samples

Table 1. Thermal characteristics of the studied compounds determined by DSC. <sup>[a]</sup>			
Compound	$\phi_{\rm p}$ [%]	Τ <sub>ιτ</sub> [°C] Heating	$\Delta H_{\rm tr}$ [kJ mol <sup>-1</sup> ] Cooling
3a (C <sub>6</sub> ) 3b (C <sub>12</sub> ) 3c (C <sub>16</sub> )	61.5 74.5 79.2	Cr <sub>ort</sub> 131.2(18.5)I Cr49.2(4.7)Col <sub>h</sub> 115(52.3)I Cr <sub>1</sub> 16.7(12.4)Cr <sub>2</sub> 42.9 Cr <sub>mon</sub> 83.2- (6.7)Cr <sub>mon</sub> 112.9(38.6)I	$\begin{array}{l} \text{I62.1}(-12.1)\text{Cr} \\ \text{I88.3}(-47.9)\text{Col}_{h}\text{43.1}(-5.7)\text{Cr} \\ \text{I70.3}(-39.5)\text{Cr}_{2}39.7(-8.4)\text{Cr}_{1} \end{array}$
[a] Cr = crystalline phase with unknown symmetry, Cr <sub>ort</sub> = orthorhombic crystalline phase, Cr <sub>mon</sub> = monoclinic crystalline phase, Col <sub>h</sub> = hexagonal phase, I = isotropic phase. The phases were assigned on the basis of X-ray diffraction data. $\phi_p$ is the volume fraction of the alkyloxy chains (C <sub>n</sub> H <sub>2n+1</sub> O): $\phi_p = 3M_p/M_w$ where $M_p$ is the molecular weight of one alkyloxy (C H <sub>2</sub> ,O) chain ( $n = 6$ , 12, 16), and $M_w$ is the molecular			

show structures close to those of the studied films. Thus, the DSC results corresponding to the bulk materials can correlate with the structural evolution occurring in thin films. The phase diagrams of the bulk compounds will be discussed in a forth-coming publication.<sup>[39]</sup> The DSC and X-ray diffraction data show that compounds **3a**, **3b** and **3c** exhibit various crystal-line and liquid-crystalline structures. Long alkyl chains favor formation of thermotropic liquid-crystalline states. To understand the interplay between the formation of H-bonds and organization of the alkyl chains, the order–disorder transition enthalpy was plotted as function of alkyl chain length (Figure 8). The DSC and X-ray diffraction data consistently show that the isotropization temperature of the studied compounds is around 115 °C, regardless of the aliphatic chain length. There-

weight of the compound.



**Figure 8.** Enthalpy variation associated with the order–disorder transition as a function of aliphatic chain length. The full and empty circles stand for melting and recrystallization, respectively. (The data for the homologous  $C_8$  compound will be discussed in a forthcoming paper<sup>[39]</sup>.)

fore, the ordered structure is mainly stabilized by the H-bond network. The enthalpy of isotropization increases with increasing length of the alkyl chains and reaches a maximum value for **3b**, which forms a columnar structure (Figure 8). Probably, the LC phase stability at high temperature is related to the number of monodendrons associated within one aggregate. In the Col<sub>h</sub> phase of **3b** the disklike aggregate is composed of six molecules, whereas for **3a** and **3c** this number is two.

#### 2.3. Ultrathin Film Morphology

Morphological analysis of spin-coated films (thickness of several tens of nanometers) deposited on silicon oxide substrates revealed a strong effect of sidechain length on the molecular orientation. In some instances, specific interactions with the substrate can result in epitaxially driven growth of a 2D structure.<sup>[28,37]</sup> Consequently, it is important to address the self-assembly of monolayers of compounds **3 a–c** on well-defined substrates such as HOPG.

Compound **3a** with short alkyl chains exhibits interesting structures. The SFM images measured on the as-prepared film deposited on silicon oxide sub-

strate show formation of columns (Figure 9, top left). To monitor structure formation and evolution in real time, the novel peak force tapping (PFT) mode was used. Operation in PFT



**Figure 9.** SFM images  $(2 \times 2 \ \mu m)$  of **3 a** measured on silicon oxide and HOPG substrates. Peak force tapping height images on silicon oxide (top): as-prepared film (left) and the same film area after annealing for 150 min at room temperature (right). Tapping-mode height images on HOPG (bottom): as-prepared film (left) and the same film after 1 h at room temperature (right). The white arrows indicate the metastable helical ribbons. The green and red triangles correspond to the same points on the images and on the height profiles.

mode allows the maximum interaction force between the SFM tip and the sample surface to be controlled, and thereby damage to such soft and fragile samples to be reduced. By performing repeated PFT measurements on the same surface area, it was found that, upon annealing for 150 min at room temperature, the columnar structure transforms into a lamellar structure, visible as high terraces in Figure 9 (top right). The thickness of a single lamellar layer of 2.0 nm corresponds to half of the *a* parameter of the crystal phase, as found from GID (Figure 2). The SFM measurements performed on the as-prepared film deposited on HOPG substrate show columnar features similar to those found on silicon oxide (Figure 9, bottom). However, for the columns, a helixlike superstructure with a height of 2.6 nm and a helical pitch of 13.2 nm can be observed in higher resolution images (indicated by a white arrow in Figure 9, bottom left). The random orientation of the helical ribbons excludes their growth by an epitaxial mechanism. The origin of the helical features remains unclear. It is possible that formation of this morphology is induced by chirality of the Lalanine head. Like the film prepared on silicon oxide, this morphology is found to be metastable and transforms to the lamellar structure after annealing for about 1 h at room temperature. The lamellar thickness is close to corresponding value for the lamellae grown on silicon oxide. The structure of the stable phase is thus independent of the nature of the substrate.

The molecules of **3 b** also self-assemble on HOPG by forming well-defined columnar structures (Figure 10). The SFM image shows that the columns are characterized by an in-plane periodicity of 4.6 nm. This repeating length is close to the unit-cell parameter of the hexagonal phase determined by GID at 60°C (Figure 4). However, this texture was found to be stable and does not evolve with time at room temperature. The columnar phase in monolayers is preserved at room temperature, probably due to spatial constraints preventing transformation of the film into the stable lamellar structure. The columns oriented parallel to the HOPG surface are regularly packed, but their inplane orientation is random, which excludes epitaxial growth mechanisms of **3b** on the graphite. Probably, in this case the adlayer promotes the planar orientation of the mesostructure on HOPG surface. This is known to occur when the structure of the adlayer differs from or is incompatible with the organization of the molecules in thin film.<sup>[37]</sup> Importantly, a fully identical structure of **3b** was also observed on SiO<sub>2</sub> surface (not shown here), which means that the observations are not specific to HOPG.

Compound **3c** forms a layer with an average thickness of 3.3 nm (high terraces in Figure 11, left). The layer thickness is close to 120 peak *d* spacings of the corresponding 3D lattice. Thus, on HOPG **3c** forms a texture with edge-on oriented molecules similar to that on silicon oxide. In addition, thinner areas can be identified, which are visible as low terraces in the images of Figure 11. A detailed analysis of the high-magnification image recorded on such a low terrace reveals in-plane organization of the molecules in a 2D monoclinic unit cell (Figure 11, right). The calculated FFT function shows a 12-spot pattern corresponding to three orientations of the 2D lattice





Figure 10. SFM image of a thin film of 3 b on HOPG, which shows a columnar structure (top). The power spectral density and a scheme of the structure of the adsorbed layer (bottom).



**Figure 11.** SFM height image of **3c** on HOPG indicating different textures: flat-on molecules visible as dark regions and edge-on molecules appearing brighter (left). High-magnification image of the dark region boxed in the left panel with the fine structure of the monolayer (right). The colored arrows indicate three orientations of the *a* axis of the 2D lattice on HOPG. The inset shows the FFT of the image. The color of the parallelograms shown on the FFT pattern is identical to the color of the arrow positioned on the corresponding single-crystal-like domain.

with the following parameters: a=6.2, b=5.9 nm, and  $\gamma=82^{\circ}$  (cf. the inset of Figure 11, right). The area of the 2D unit cell of 36.1 nm<sup>2</sup> is close to the *ab* projection of the corresponding 3D unit cell (37.8 nm<sup>2</sup>) measured in thin film at room temperature. Thus, the molecular arrangement in the 2D monoclinic lattice is close to that in the (001) plane of the crystalline phase

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found in thin films on silicon oxide (Figure 7). A small deformation of the unit cell can probably be accounted for by the interaction with the substrate. In our previous work, we showed that epitaxy to graphite can significantly modify the 2D structure of wedge-shaped molecules (3,4,5-tridodecyloxycinnamic acid) due to the tendency of alkyl chains to extend along the [100] direction of HOPG.<sup>[28]</sup> The angle of 60° between the *a* axes of the crystals shows the epitaxial character of monolayer growth on the HOPG surface.

Taking into account similar molecular shapes of 3,4,5-tridodecyloxycinnamic acid studied previously and **3 c**, one can suggest that the hexadecyloxy side groups are also oriented parallel to the principal axes of HOPG. However, due to the alternating orientation of the alkyl chains in the bulk structure of **3 c**, one can suppose that on the surface the side groups are oriented along both [100] and [010] directions of HOPG (Figure 12). The observed 2D structure can be considered as an adlayer on which a thicker film is formed. However, no epitaxial relations between the 2D lattice and the lattice of the thick film structure addressed by GID were found.



Figure 12. Schematic representation of a 2D lattice of 3 c on the HOPG surface. The orientation of HOPG with respect to the lattice of 3 c is indicated.

Generally, for discotic molecules on silicon oxide<sup>[40]</sup> and HOPG<sup>[19]</sup> substrates the planar film texture is considered to be metastable due to higher surface energy of the molecular cores. For molecules **3a** and **3b** the high surface energy of alanine competes with the tendency of the alkyl chains to lie parallel to HOPG. For the molecule with the longest side groups, that is, **3c**, the role of the alkyl chains in structure formation becomes dominant. In contrast, the alkyl chains of **3a** and **3b** do not exhibit the epitaxial growth mode of the corresponding 2D self-assemblies.

### 3. Conclusions

Structural studies on *N*-[3,4,5-tris(alkyloxy)benzoyl] L-alanines **3a-c** demonstrate that the length of the alkyl side chains ( $C_6$ ,  $C_{12}$ ,  $C_{16}$ ) dramatically affects the morphology and thermotropic behavior of the compounds in thin films. Compound **3a** ( $C_6$ ) exhibits a layerlike orthorhombic crystalline structure, which transforms into a monoclinic phase during heating. Compound **3b** with longer alkyl groups forms a layerlike crystal structure

at room temperature which is similar to that of **3a**. However, at higher temperatures this phase transforms into a liquid-crystalline hexagonal columnar phase  $Col_h$  with columns parallel to the substrate. Further increase of the side-chain length to  $C_{16}$  (**3c**) leads to crystallization in the columnar rectangular lattice with alternating orientation of alkyl chains parallel to the substrate. Heating of sample **3c** results in formation of a layerlike liquid-crystalline phase. All samples exhibit close isotropization temperatures indicating the formation of H-bonds.

The SFM measurements on monolayers of **3a–c** on HOPG surface show that the monodendrons with  $C_6$  and  $C_{12}$  side chains self-assemble into 2D lattices with parameters close to those found for thick films. In contrast, the sample with the longest alkyl groups self-organizes in a monoclinic 2D structure formed by flat-on oriented molecules. The molecular packing in the monolayer is in this case similar to the *ab* plane of the corresponding 3D crystalline phase formed in thick films but is oriented at 90° with respect to the thick-film structure. The structure modification in the monolayer is governed by the epitaxial growth mode of the 2D lattice due to the strong interaction of the long alkyl chains with the graphite substrate.

Variation of the ratio between the polar core and aliphatic periphery allows the role of each constitutive unit in structure formation to be understood. The alanine molecular tip provides for formation of the molecular clusters which play the role of building blocks for the 2D and 3D self-assembly. The length of linear alkyl groups is a very sensitive parameter providing control of the film texture and polymorphic behavior. Thus, the choice of the alkyl chain length can be used to induce the formation of molecular aggregates of particular shape and also to design desired film textures.

### **Experimental Section**

Materials: 1-Bromododecane (97%), thionyl chloride (99+%), ethyl 3,4,5-trihydroxybenzoate (98%), L-alanine methyl ester hydrochloride, anhydrous potassium carbonate, and potassium hydroxide were obtained from Aldrich and used as received. Dimethylformamide (DMF) was dried over calcium hydride for 12 h and distilled under vacuum. Concentrated hydrochloric acid (37%), triethylamine, ethanol, dichloromethane, and chloroform were purchased from Fluka. L-Alanine hydrochloride was pursued from Aldrich. 3,4,5-Tris(alkyloxy)benzoyl chlorides 1a-c were prepared according to a literature procedure.<sup>[34]</sup>

*N*-[3,4,5-Tris(hexyloxy)]benzoyl L-Alanine Methyl Ester (**2 a**): Freshly prepared acid chloride **1 a** (0.64 g, 1.45 mmol) was dissolved in chloroform (40 mL), and L-alanine methyl ester hydrochloride (0.18 g, 1.45 mmol) was added. The resulting mixture was cooled to 0 °C, and then a solution of triethylamine (0.3 g, 2.90 mmol) in chloroform (5 mL) was added dropwise while the temperature was kept below 5 °C. The reaction mixture was stirred at room temperature overnight. Afterwards it was diluted with chloroform (150 mL), and the solution washed three times with distilled water (50 mL). The organic phase was separated, the solvent evaporated, and the residue dried in vacuo. A slightly yellow solid was obtained. Yield: 85 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS/300 MHz):  $\delta$  = 1.23 (t, 9 H), 1.33 (overlapping, m, 18 H), 1.81 (m, 6H), 3.79 (s, 3 H), 4.77 (q, 1 H), 6.67 (d, 1 H), 7.00 ppm (s, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>/TMS/75 MHz):  $\delta$  = 14.0, 14.1, 18.6,

22.6, 22.7, 25.7, 29.3, 25.7, 29.3, 30.2, 31.5, 45.4, 48.5, 52.6, 53.4, 69.3, 73.4, 105.8, 128.8, 141.4, 153.1, 166.7, 173.8 ppm.

*N*-[3,4,5-Tris(dodecyloxy)]benzoyl L-Alanine Methyl Ester (**2b**): The synthesis was carried out according to the same procedure as for **2a**. A slightly yellow solid was obtained. Yield: 88%. <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS/300 MHz):  $\delta$  = 0.88 (t, 9H), 1.27 (m, 54H), 1.50 (d, 3H), 1.81 (m, 6H), 3.79 (s, 3H), 4.00 (m, 6H), 4.77 (m, 1H), 6.69 (d, 1H), 7.00 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>/TMS/75 MHz):  $\delta$  = 14.1, 18.6, 22.7, 26.1, 29.4, 29.6, 29.6, 29.7, 30.3, 31.9, 48.5, 52.5, 69.4, 73.5, 105.8, 128.8, 141.4, 153.1, 166.7, 173.8 ppm.

*N*-[3,4,5-Tris(hexadecyloxy)]benzoyl L-Alanine Methyl Ester (**2** c): The synthesis was carried out according to the same procedure as for **2a**. A slightly yellow solid was obtained. Yield: 80%. <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS/300 MHz):  $\delta$  = 0.88 (t, 9H), 1.26 (overlapping, m, 81H), 1.81 (m, 6H), 3.79 (s, 3H), 4.00 (t, 6H), 4.80 (q, 1H), 6.66 (d, 1H), 6.99 ppm (s, 2H).

*N*-[3,4,5-Tris(hexyloxy)]benzoyl L-Alanine (**3a**): Compound **2a** (1 g, 1.97 mmol) and KOH (0.44 g 7.88 mmol) were dissolved in a mixture of ethanol (30 mL) and water (5 mL). The solution was heated to reflux for 12 h and then cooled to about 40 °C. Afterwards, it was acidified with concentrated hydrochloric acid (37%) to pH 1. The resulting precipitate was filtered off and dried in vacuo. After recrystallization from ethyl acetate a white solid was obtained. Yield: 93%. <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS/300 MHz):  $\delta$  = 1.33 (t, 9H), 1.32 (overlapping, m, 21 H), 1.80 (m, 6H), 4.02 (m, 6H), 4.77 (q, 1 H), 6.79 (d, 2 H), 7.00 ppm (s, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>/TMS/75 MHz):  $\delta$  = 14.0, 14.1, 18.2, 22.6, 22.7, 25.8, 29.3, 30.3, 31.6, 31.7, 48.8, 69.4, 73.6, 76.6, 77.1, 77.5, 105.9, 128.2, 141.6, 153.2, 167.6, 176.7 ppm.

*N*-[3,4,5-Tris(dodecyloxy)]benzoyl L-Alanine (**3 b**): The synthesis was carried out by the same procedure as for **3 a**. Pure compound **3 b** was obtained without recrystallization. Yield: 87%. <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS/300 MHz):  $\delta = 0.88$  (t, 9H), 1.27 (m, 54H), 1.57 (d, 3H) 1.77 (m, 6H), 3.99 (m, 6H), 4.76 (m, 1H), 6.80 (d, 1H), 6.99 ppm (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>/TMS/75 MHz):  $\delta = 14.1$ , 18.2, 22.7, 26.1, 29.4, 29.5, 29.7, 29.7, 30.3, 32.0, 48.9, 69.4, 73.6, 105.9, 128.2, 141.7, 153.2, 167.7, 176.5 ppm.

*N*-[3,4,5-Tris(hexadecyloxy)]benzoyl L-Alanine (**3** c): The synthesis was carried out by the same procedure as for **3** a. Yield: 91%. <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS/300 MHz):  $\delta$ =0. (t, 9H), 1.26 (overlapping, m, 81H), 1.76 (m, 6H), 4.00 (t, 6H), 4.80 (q, 1H), 6.77(d, 1H), 6.99 ppm (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>/TMS/75 MHz):  $\delta$ =14.1, 18.2, 22.7, 26.1, 29.4, 29.5, 29.7, 29.7, 30.3, 32.0, 48.9, 69.4, 73.6, 105.9, 128.2, 141.7, 153.2, 167.7, 176.5 ppm.

Characterization: <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were recorded on a Bruker DPX-300 spectrometer in  $CDCI_3$  with TMS as internal standard at 20 °C.

Thermal polarizing optical microscopy analysis was performed on A Zeiss Axioplan 2 polarizing microscope, equipped with METTLER FP 90 hot stage. Images were taken from a digital Zeiss AxioCam MRC4 camera in combination with the Zeiss AxioVision software.

Differential scanning calorimetry (DSC) measurements were performed by using a Netzsch DSC 204 unit. Samples (typical weight: 5 mg) were enclosed in standard Netzsch aluminum crucibles. Indium and palmitic acid standards were used for calibration. The heating and cooling rates were  $10^{\circ}$ Cmin<sup>-1</sup>. Grazing incidence X-ray diffraction (GID) experiments were conducted on the ID10B beamline of the ESRF at a wavelength of 1.55 Å and incidence angle of  $0.2^{\circ}$ . The samples for GID were prepared by spin coating of 10 mg mL<sup>-1</sup> solution in chloroform on cleaned silicon wafers. The scattering was recorded with a MAR CCD camera.

Scanning force microscopy (SFM) was use to investigate the surface morphology of the films at room temperature with a Nanoscope V controller. The imaging was done in tapping mode with standard silicon cantilevers: Nanoworld Pointprobe NCH 330 or 75 kHz and super-sharp tips from µ-Masch. The films were prepared by spin coating with rotation speed of 2000 rpm of approximately 40  $\mu L$  of chloroform solutions with concentrations of 1 wt % onto freshly cleaved HOPG substrates or precleaned SiO<sub>2</sub> surface. During operation in the recently developed peak force tapping (PFT) mode,<sup>[41]</sup> a feedback maintains a constant peak force, which can be as low as several piconewtons. This approach is based on acquisition of force curves recorded at each moment of the tipsample interaction, which enables the nanomechanical properties to be quantitatively assessed if the cantilever spring constant and tip shape are calibrated. The cantilevers used for the measurements in PFT mode were SNL-B with spring constant of about  $0.3 \ \mathrm{Nm^{-1}}$  (Bruker Probes). The peak force set point was fixed at 1 nN.

### Acknowledgements

The authors acknowledge the French Agence Nationale de la Recherche for financial support in the frame of SPIRWIND project (HABISOL program) and T2T project (Blanc International program). This work was supported by the European Commission within FP7 Marie Curie Initial Training Network "HIERARCHY" (Project Reference: 215851). The authors are grateful to the Russian Ministry of Science and Education (project for financial support of leading scientists No. G34.31.0055 from 19.10.2011) for financial support.

Keywords: hydrogen bonds  $\cdot$  liquid crystals  $\cdot$  monodendrons  $\cdot$  self-assembly  $\cdot$  thin films

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Received: September 22, 2011 Revised: February 1, 2012 Published online on March 7, 2012