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From Macro- to Nanoscopic Templating with Nanographenes

Wojciech Pisula,† Marcel Kastler,† Daniel Wasserfallen,† Richard J. Davies,§
Mari-Cruz García-Gutiérrez,‡ and Klaus Müllen*,†

Max-Planck-Institut für Polymerforschung, 55128 Mainz, Germany, European Synchrotron Radiation Facility,
B.P. 220, F-38043 Grenoble Cedex, France, Instituto de Estructura de la Materia, C.S.I.C.,
Serrano 121, 28006 Madrid, Spain

Received June 14, 2006; E-mail: muellen@mpip-mainz.mpg.de

Controlling the organization of organic semiconductors through nanoobject manipulation is highly desirable for device miniaturization, but remains a challenging task. For different organic materials it has already been shown that templating is one solution which allows the creation of structures with nanoscopic dimensions.[1] For example, microporous inorganic templates can produce one-dimensional arrays using alumina membranes having a well-defined pore diameter.[2] After the material is molded[3] or solution deposited[4] into the pores, the inorganic template is carefully removed. The resulting tubular nanoobjects possess a highly regular and well-defined structure.[5] The structure of the objects can be controlled by modifying the geometric confinement of the pores.[6] This technique is an alternative to the fabrication of graphite nanotubes and -rods, which are prepared by pyrolysis of the prealigned organic material within the pores.[7]

Discotic liquid crystals are especially important for templating applications because of their unique self-assembling propensity. This results in highly ordered superstructures which can arrange on interfaces face- and edge-on. Consequently, they have considerable potential as organic semiconductors.[8] Wendorff et al. recently reported the alignment of a triphenylene derivative from the melt within pores of different sizes and determined an optimal pore diameter for the orientation.[9]

In this work, we present the spontaneous self-alignment of an extended polycyclic aromatic hydrocarbon, namely a hexa-*peri*-hexabenzocoronene (HBC) (**1**), within macro- and nanoscopic pore-like templates by melt processing. The aromatic HBC core is 6-fold substituted by long, branched 2-decyl-tetradecyl ($C_{14,10}$) alkyl side chains which provide a low isotropization temperature of 46 °C.[10] During slow cooling from the melt, the compound forms large spherulites, several hundred micrometers in size, with radially oriented columnar structures and an edge-on molecular arrangement.[10a] It will be shown that this pronounced directional growth of the molecules is essential for successful nano- and macroscopic templating. In comparison to previously reported template-induced alignment of triphenylenes,[9b] it was possible to obtain a uniform orientation of **1** over even several centimeters.

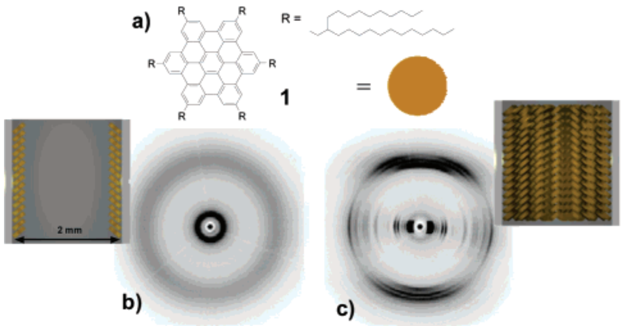

Figure 1. (a) Chemical structure of **1**; spontaneous self-assembly of **1** from the isotropic state within a two millimeter thick capillary; (b) 2D-WAXS pattern of the isotropic phase and (c) after controlled cooling down to room temperature. The schematic inset in parts b and c illustrates the supramolecular organization in the corresponding temperature.

In the first approach, **1** was placed in a glass capillary with a diameter of two millimeters and heated to the isotropic phase. Two-dimensional wide-angle X-ray scattering (2D-WAXS) experiments confirmed that the material was molten, exhibiting isotropic scattering (the capillary was positioned vertical with its axis to the detector) (Figure 1b). After cooling to room temperature at a rate of 1 °C/min, the structure of the sample was reinvestigated by 2D-WAXS. On this occasion, sharp and distinct reflections appeared indicating both a high supramolecular order and pronounced long-range orientation. The organization was identical along the entire capillaries length. Reflections in the equatorial plane of the X-ray pattern relate to a uniaxial orientation of the columns along the capillary axis. Meanwhile the off-axis reflections are characteristic of a tilted intracolumnar arrangement of the discs. This organization was in strong accordance with the bulk order of mechanically extruded filaments (Supporting Information, Figure S1). Because of the considerable scaling difference between the capillaries diameter and molecular length-scales, it was assumed that the curvature effect of the capillary has no influence on the macroscopic self-organization of the discs. Indeed, nucleation is probably initiated at the air-material interface with crystallization proceeding along the capillary as the temperature further decreases. The resulting thermal gradient leads to the final extraordinary self-assembly of the columnar structures over long-ranges. This orientation effect was supported by the apparent directional self-assembly propensity of **1**, as observed already in the spherulite growth. On the other hand, the arrangement of the first monolayer at the surface was important for the internal organization. A similar mechanism has been suggested for the macroscopic self-organization of discotics during the formation of homeotropic phases.[11] In our case, the first molecules initially wetted the capillary wall in an edge-on arrangement with respect to the capillary wall as illustrated schematically in Figure 1a. During further crystallization additional molecules interacted with the already aligned discs at the wall resulting in an identical organization in the interior of the capillary.

To evaluate the self-assembly on the nanoscale, the pronounced directional growth and low nucleation propensity of **1** was studied in inorganic membranes possessing much smaller pore diameters (sample preparation is described in the Supporting Information). Using scanning electron microscopy (SEM), the membrane pores could be visualized before and after filling. These images revealed

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† Max-Planck-Institut für Polymerforschung.
‡ European Synchrotron Radiation Facility.
§ Instituto de Estructura de la Materia.

10.1021/ja0641960 CCC: $33.50

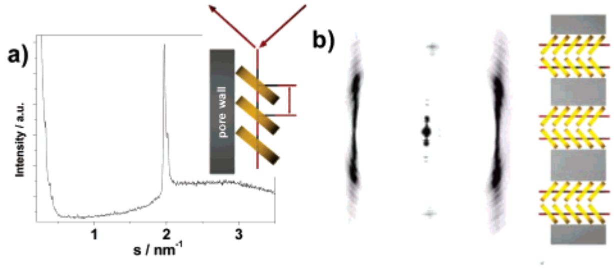

Figure 2. (a) Large-area X-ray diffraction in reflection mode of the templated **1** (the schematic drawing illustrates the orientation of the scattering vector with respect to the columnar and molecular organization at the pore wall); (b) synchrotron microfocus X-ray diffraction pattern recorded with a beam perpendicular to the pores with the aligned material; the illustration displays the organization indicated by the X-ray pattern.

that the pores were completely filled with the compound over the whole length (Supporting Information, Figure S2).

X-ray diffraction allowed the degree of supramolecular order to be investigated within the nanopores after thermal processing. Figure 2a shows a large-area X-ray diffraction pattern collected in a reflection geometry. One single distinct reflection appeared in the diffractogram corresponding to a repetition distance of 0.49 nm. This distance was related to the intracolumnar period of discotic molecules tilted by ca. 45°. The schematic drawing in Figure 2a illustrates the parallel orientation of the scattering vector with respect to the columnar axes.

As an additional technique, microfocus synchrotron radiation X-ray experiments (beam spot size at the focal position ca. $0.8 \times 0.8\ \mu m^2$) were performed at the ID13 beamline (ESRF). The synchrotron beam was carefully aligned perpendicular to the pore channels and the 2D-WAXS patterns were recorded (Figure 2b). The pattern was found to be identical to the one obtained from the macroscopically organized material confirming the orientation of the columnar structures along the membrane pores. Moreover, the larger number of higher order reflections and their sharp, distinct shapes indicated an improved supramolecular order of **1**. No misalignment of the columnar orientation could be observed from the X-ray pattern confirming the perfection of the self-assembled structures. In contrast, the 2D-WAXS conducted in transmission (beam size ca. 1 mm) along the pores (and thus along the stacking axes) revealed only intercolumnar correlations and no reflections resulting from periodicities between the interacting molecules (Supporting Information, Figure S3). In principle, the curvature on a much smaller dimension in comparison to the capillary could have an additional effect on the order. However, it is more probable that, similar to the macroscopic alignment, a crystallization gradient leads to the pronounced organization in the pores.

To insulate the templated objects and to obtain nanorods possessing the pronounced organization, the aluminum oxide membrane was carefully dissolved in an aqueous, dilute, cold sodium hydroxide solution. This procedure was necessary because of the exothermic reaction during the dissolving process and the low isotropization temperature of **1**. SEM images taken after the complete removal of the inorganic template depicted intact, organized nanofibers of **1** (Figure 3). Because of the relatively large deformability of the solid material (plastic crystalline phase) and the waxy state at room temperature of **1**, the fibers arrange into bundles of rods, possessing a length-to-thickness ratio which is too high for them to be free-standing.

In conclusion, the extraordinary self-organizational capability of **1** allowed templating of the material macro- and nanoscopically, accompanied by a high degree of long-range supramolecular orientation. No significant effect of the diameter of the template cannel (and thus of the curvature on the supramolecular order) was observed in this work, as reported for triphenylenes.[9b] This is the first example for the spontaneous self-assembly of a discotic system which occurs uniformly over such macroscopic dimensions. This opens a variety of potential applications. One possibility might be the introduction of **1** as donor material into porous titanium dioxide for applications in photovoltaic cells. The aligned columnar structures might ensure an undisturbed charge carrier transport to the electrodes after charge separation.[12]

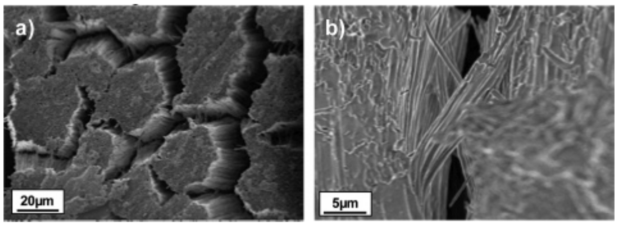

Figure 3. SEM images illustrating nanorods after the removal of the inorganic template organized in (a) bundles and (b) single structures.

Acknowledgment. The authors acknowledge financial support from the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm: Organische Feldeffekt-Transistoren) and the EU project NAIMO (Integrated Project Number NMP4-CT-2004-500355). M.K. thanks the Fonds der Chemischen Industrie for graduate fellowships.

Supporting Information Available: Experimental procedures, 2D-WAXS patterns of the bulk material and of the membrane, and SEM images of the membranes before and after filling. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0641960