

Liquid Crystals

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Ordered Nanostructures from the Self-Assembly of Reactive Coil–Rod–Coil Molecules\*\*

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One of the most important challenges in the areas of nanomaterials and biomimetic chemistry is to construct supramolecular structures with well-defined shape and size

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by the self-assembly of programmed molecules.<sup>[1]</sup> Control of the supramolecular structure of self-assembling molecules and subsequent cross-linking of specific segments within the organized structure are an efficient way to produce robust organic nanomaterials while maintaining the precise size and shape of the self-assembled nanostructure.<sup>[2]</sup> Rod-shaped molecules containing flexible chains have been shown to self-assemble into a large variety of supramolecular structures, which include 3D bicontinuous cubic and 2D columnar structures.<sup>[3]</sup> To enhance the structural robustness of the self-assembled nanoarchitectures, we designed a coil–rod–coil molecule that contains polymerizable vinyl groups in the middle of the rod segment. Herein, we describe the self-assembling behavior of the coil–rod–coil molecule, **1** (Figure 1), which bears reactive divinyl groups in the center of the rod block, and the subsequent polymerization of **1** from an ordered state.

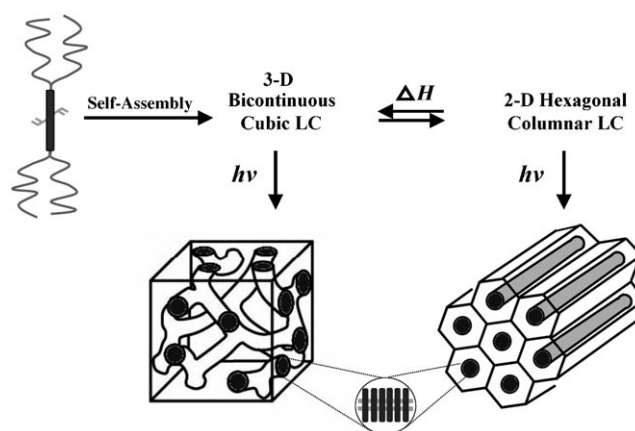
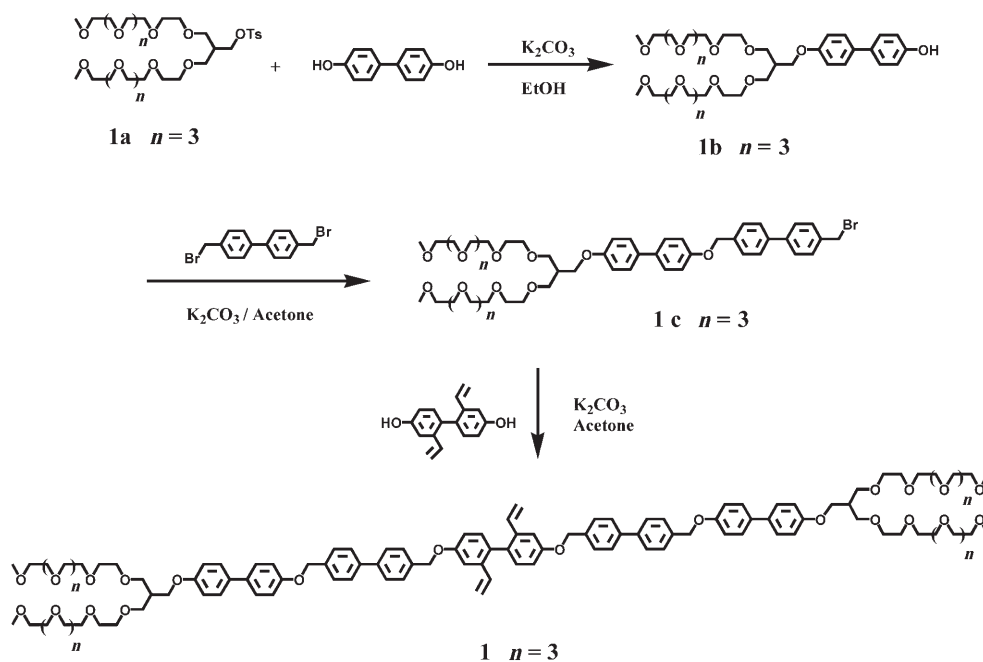


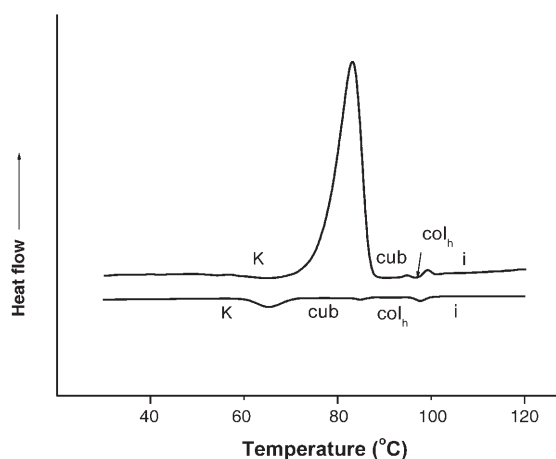
Figure 1. Schematic representation of liquid crystalline phases of **1** and subsequent polymerization to yield ordered nanostructures.

The triblock molecule, **1**, consisting of five biphenyl units linked through benzyl ether linkages and bis(pentaethylene glycol) dendrons as coil segments at both ends of the rod, was synthesized by etherification of penta(ethylene glycol) mono-methyl ether and 4,4'-biphenol, and the resulting product was subsequently treated with excess 4,4'-bis(bromomethyl)biphenyl to obtain a white waxy solid, **1c** (Scheme 1). Simple etherification of **1c** with 2,2'-divinyl-4,4'-biphenol in the presence of K<sub>2</sub>CO<sub>3</sub> afforded **1**. The final product was characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy and by elemental analysis. The results were in full agreement with the structure presented in Scheme 1.

The mesophase structure of **1** was investigated by differential scanning calorimetry (DSC), thermal optical polarized microscopy, and small-angle X-ray scattering (SAXS). On heating, **1** melts into a liquid crystalline phase at 83 °C and then converts into a second liquid crystalline phase which, in turn, undergoes isotropization at 99.5 °C (Figure 2). On slow cooling from the isotropic liquid phase, first a spherulitic texture is observed and finally pseudofocal conic domains develop, which is characteristic of a hexagonal columnar mesophase. On further cooling from the hexagonal columnar



**Scheme 1.** Synthesis of **1**.

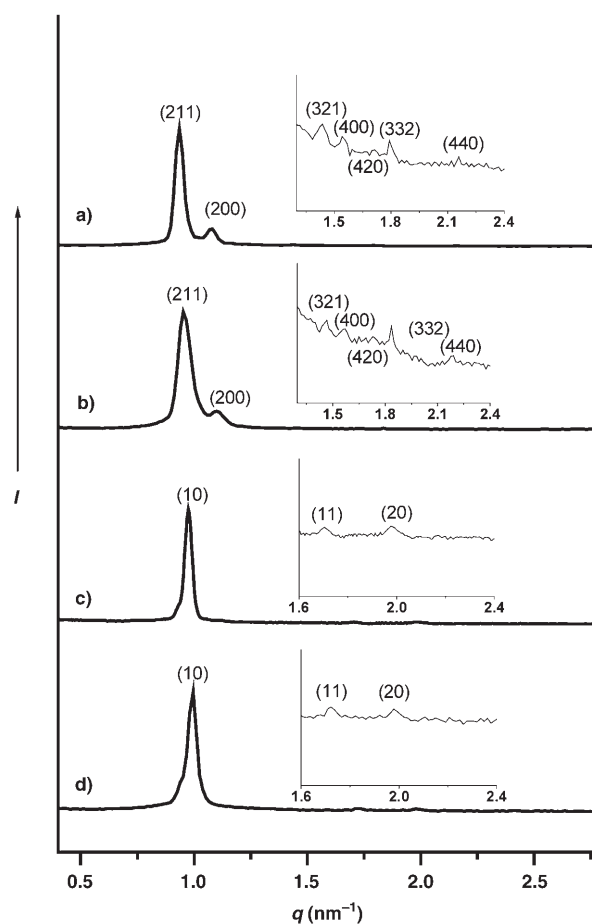


**Figure 2.** DSC traces of **1** recorded during the heating and cooling scans (K=crystalline, cub=cubic, col<sub>h</sub>=hexagonal columnar, i=isotropic phase).

phase, the birefringent texture disappears completely, thus indicating the presence of a cubic mesophase (see Supporting Information).<sup>[4]</sup> When **1** is in the optically isotropic liquid crystalline phase, the corresponding small-angle X-ray diffraction patterns show a number of sharp reflections (Figure 3 a), which can be indexed as a bicontinuous cubic order ( $Ia\bar{3}d$  symmetry) with a lattice constant  $a = 16.5$  nm.<sup>[3b,5]</sup> At a wide angle, only a diffuse halo remains as evidence of the lack of any positional long-range order other than the 3D cubic packing of supramolecular units (see Supporting Information). In the birefringent liquid crystalline phase at higher temperature, the SAXS patterns show three sharp reflections that can be assigned as the (10), (11), and (20) reflections of a hexagonal columnar structure with a lattice constant  $a =$

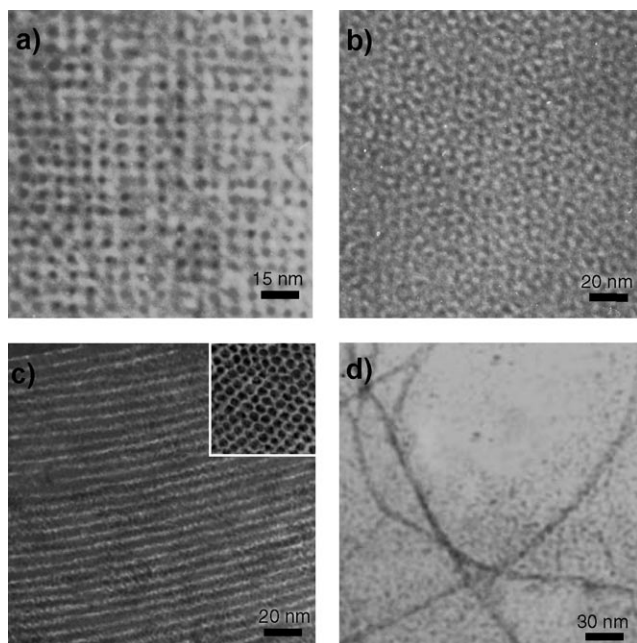
7.4 nm (Figure 3 c).<sup>[3]</sup> These results, together with optical microscopic observations, indicate that **1** exhibits 3D bicontinuous cubic and hexagonal columnar liquid crystalline phases.

The polymerization of **1** in the liquid crystalline state provides a strategy for constructing well-defined nano-objects if the polymerization proceeds with retention of a liquid crystalline structure. To demonstrate this concept, the photopolymerization of **1** was performed at various liquid crystalline states, with 2,2-dimethoxy-2-phenylacetophenone being used as a photoinitiator. After photopolymerization in each



**Figure 3.** Representative SAXS spectra: a) bicontinuous cubic structure of **1**; b) bicontinuous cubic structure after polymerization at 85 °C; c) hexagonal columnar structure of **1**; d) hexagonal columnar structure after polymerization at 97 °C.

liquid crystalline phase, FTIR spectroscopy clearly showed that the peaks assigned to the out-of-plane bending band of C–H in the vinyl group at 919 and C=C band at 1640  $\text{cm}^{-1}$  were strongly suppressed, which is indicative of extensive polymerization (see Supporting Information).<sup>[6]</sup> The SAXS pattern of the sample after polymerization at 85 °C shows the same reflections as those of the bicontinuous cubic liquid crystalline structure of **1**. This result is consistent with the preservation of the 3D bicontinuous cubic structure upon polymerization. To corroborate the detailed nanostructures, TEM experiments were performed with the polymerized samples. The TEM images of an ultra-microtomed thin film of the samples (stained with  $\text{RuO}_4$ ) polymerized in the bicontinuous cubic liquid crystalline phase showed tetragonal and hexagonal arrays of dark rod domains in a light coil matrix along the  $[01\bar{1}]$  and  $[\bar{1}11]$  directions, respectively, which is characteristic of a 3D bicontinuous cubic structure.<sup>[7]</sup> The lattice constant, calculated to be 16 nm, is in agreement with the value estimated from the SAXS data (Figure 4 a, b). Bulk



**Figure 4.** a,b) TEM images of an ultra-microtomed thin film of the sample polymerized in the optically isotropic mesophase stained with  $\text{RuO}_4$ , which exhibit an ordered array of tetragonal and hexagonal dark rod domains in a light coil matrix along the  $[01\bar{1}]$  (a) and  $[\bar{1}11]$  directions (b); c) an ultra-microtomed thin film of the sample polymerized in the birefringent mesophase stained with  $\text{RuO}_4$ , which reveals alternating dark rod layers and light coil layers; the inset shows an in-plane hexagonally ordered array of dark rods in a coil matrix; d) dispersed nanofibers in aqueous solution (stained with  $\text{RuO}_4$ ).

polymerization of **1** at 97 °C also proceeded with retention of the hexagonal columnar liquid crystalline structure, as confirmed by SAXS and TEM (Figure 3 b and d). The SAXS pattern showed reflections similar to those of hexagonal columnar mesophase with a small lattice contraction (from 7.4 nm to 7.3 nm) as a consequence of the stitching together of rod segments. This result indicates that polymerization takes

place with retention of the 2D liquid crystalline structure. The TEM images stained with  $\text{RuO}_4$  showed a hexagonal array of dark aromatic domains in a matrix of light polyethylene oxide chains as well as views in the direction of the column. The interdomain distance appears to be approximately 7 nm, which is consistent with that obtained from the SAXS data (Figure 4c). Interestingly, when the hexagonal columnar structure was sonicated in water for several hours, the solid dispersed into individual nanofibers (Figure 4d). Thus, polymerization takes place only within the cylindrical cores. Bulk polymerization in the hexagonal columnar state gives rise to well-defined nanofibers with a uniform diameter. It should be noted that the wide-angle X-ray scatterings (WAXS) after polymerization in each liquid crystalline state showed that the reflection corresponding to 0.47 nm shifts to a slightly higher angle (0.45 nm), thus indicating that polymerization occurs with only a small degree of shrinkage. This shift is consistent with the results of very small lattice constant reductions in SAXS patterns (see Supporting Information).

Recently, there have been many reports of Suzuki couplings in water,<sup>[8a]</sup> and we have demonstrated that self-assembled aromatic rod bundles encapsulated by hydrophilic chains can be used as an efficient nanoreactor for Suzuki coupling reactions.<sup>[8b]</sup> This result motivated us to investigate whether our nanofibers are suitable to use as nanoreactors in aqueous solution because the nanofibers consist of an aromatic core surrounded by hydrophilic chains. To investigate the capability of the nanofibers as a reactor, we have performed the Suzuki coupling reaction with phenyl boronic acid and bromoanisole in the presence of the nanofibers in aqueous solution at room temperature. Remarkably, the reaction conversions were almost quantitative. This reactivity demonstrates that the nanofibers are highly efficient nanoreactors (Table 1). Owing to their covalently fixed character-

**Table 1:** Suzuki cross-coupling reaction of phenyl boronic acid and bromoanisole in a nanofiber nanoreactor.<sup>[a]</sup>

Cycle	First	Second	Third	Fourth
yield [%] <sup>[b]</sup>	95	94	93	93

[a] The reaction was carried out in water at room temperature. Reaction conditions: bromoanisole (0.1 mmol), phenyl boronic acid (0.12 mmol),  $\text{Pd}(\text{OAc})_2$  (0.5 mol %),  $\text{P}(\text{Ph})_3$  (1.0 mol %),  $\text{NaOH}$  (0.2 mmol), nanofiber (0.025 mmol),  $\text{H}_2\text{O}$  (10 mL), stirring at room temperature for 12 h. [b] Percent yields are calculated on the basis of GC analysis with xylene used as the internal standard.

istics, nanofibers can be easily recycled for use in further reactions by filtering the mixture and washing the nanofibers with ethyl acetate. As shown in Table 1, the nanofibers can be used up to four times and still maintain activity. The aqueous Suzuki coupling reactions in the presence of the nanofibers take place within the aromatic cores of the nanofibers at room temperature as these cores are able to entrap solvophobic aromatic reactants through intermolecular interactions, including hydrophobic interactions and  $\pi$ - $\pi$  interactions. This entrapment leads to a highly concentrated reaction site that lowers the energy barrier for the coupling reaction. The confinement of the aromatic substrates within the aromatic

cores of the nanofibers was confirmed by using fluorescence spectroscopy on aryl halides, boronic acids, and triphenylphosphine (see Supporting Information). Upon addition of the aromatic substrates, the fluorescence intensities of the nanofiber solutions were suppressed, thus demonstrating that they are effectively entrapped within the aromatic bundle of the nanofibers.<sup>[8]</sup>

In summary, we have synthesized a polymerizable coil-rod-coil molecule, which self-organizes into 2D columnar and 3D bicontinuous cubic structures at the liquid crystalline state. Photopolymerizations of **1** in liquid crystalline state proceeds with preservation of the ordered supramolecular architectures and maintenance of the lattice dimensions. Photopolymerization of **1** in the bicontinuous cubic liquid crystalline state gives rise to a 3D ordered nanostructure, while in the hexagonal columnar liquid crystalline state it produces a 2D ordered nanostructure that in aqueous solution can be dispersed into individual nanofibers with a uniform diameter. The remarkable feature of these nanofibers, which have aromatic cores, is their ability to be used as recyclable nanoreactors for room-temperature Suzuki coupling reactions in aqueous solution. The covalent stitching of reactive rod segments within the ordered state by photopolymerization offers a strategy to construct shape-persistent organic nanomaterials with well-defined size and shape, which potentially have applications in macromolecular electronics, nanoreactors, and hybrid nanomaterials.

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