

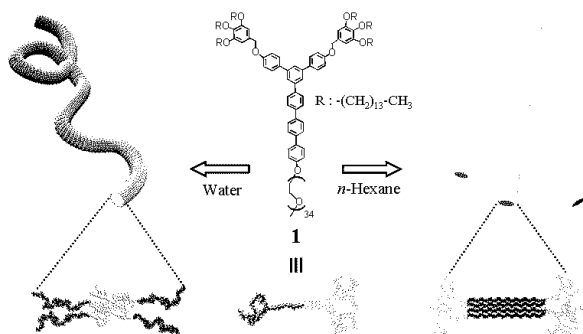
## Invertible Nanofibers with Tunable Stiffness from Self-Assembly of an Amphiphilic Wedge-Coil Molecule

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### Introduction

Self-assembly of amphiphilic block molecules can lead to a variety of nanostructures, including spherical micelles, vesicles, nanofibers, and tubes.<sup>1</sup> Among the nanostructures formed by self-assembly of programmed molecules, 1-D fibrillar assembly has been proved to be particularly interesting for applications such as nanowires, and biomimetic macromolecules.<sup>2</sup> The 1-D structures with stimuli responsive features are likely to further enhance their scope as intelligent materials. Although stimuli responsive nanostructures have been extensively studied with spherical objects,<sup>3</sup> switching the properties triggered by external stimuli with 1-D fibrillar objects remains challenging.<sup>4</sup> In this context, we have been interested in the preparation of stimuli responsive 1-D cylindrical assembly with tunable properties triggered by the solvent environment.



**Figure 1.** Schematic representation of the flexible coil-like and stiff rod-like nanofibers.

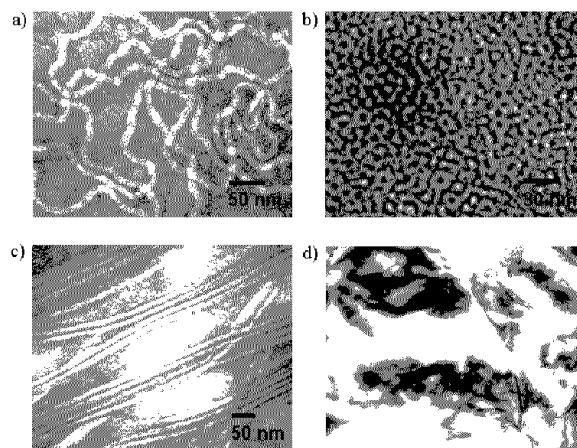
### Results and discussion

The wedge-coil molecule (**1**), when dissolved in a selective solvent for one of the blocks, can self-assemble into an aggregate structure because its amphiphilic characteristics. Dynamic light scattering (DLS) experiments were performed with **1** in water (0.01 wt%), a selective solvent for the poly(ethylene oxide) chains and *n*-hexane (0.01 wt%), a selective solvent for the hydrophobic wedge segments in order to investigate the aggregation behavior. The wedge-coil molecule shows aggregation behavior in both water as well as *n*-hexane, as evidenced by autocorrelation functions.

The evidence for the formation of the cylindrical aggregates in both polar and apolar solvents was also provided by transmission electron microscopy (TEM) experiments (Figure 2). The micrographs with negatively stained with a 2 wt% aqueous solution of uranyl acetate show highly curved cylindrical objects in a uniform diameter of about 15 nm, indicating the formation of flexible coil-like nanofibers. To get more information of these nanofibers, we have additionally performed TEM experiments with an ultramicrotomed film dried from aqueous solution (positively stained with RuO<sub>4</sub>). The cross-section image of the fibers showed more stained dark aromatic domains surrounded by lighter PEO segments. The diameter of the core was measured to be approximately 5 nm, which is estimated length of an aromatic part together with a tetradecyl group (5.4 nm by CPK).

Similar to the aqueous solution, the wedge-coil block molecule in *n*-hexane was also observed to form cylindrical objects. However, the curvature of the cylindrical micelles formed in *n*-hexane shows to be significantly different from that in water. The micrographs positively stained from RuO<sub>4</sub> showed bundles of the cylindrical aggregates aligned parallel to each other. These cylinders have lengths up to several micrometers and a uniform diameter of about 16 nm. Notably,

there is obvious contrast between the periphery and center in the cylindrical object, indicating that the cylinders consist of light coil interior and dark aromatic exterior in *n*-hexane solution.<sup>5</sup> Considering the extended molecular length (13.8 nm by CPK), the diameter of 16 nm indicates that the PEO chains within the core are fully interdigitated with each other. The formation of bundles of the micelles could be attributed to the existence of stiff rod-like micelles. Because rod-like shape with a high aspect ratio is a crucial prerequisite to form a liquid crystalline ordering,<sup>6</sup> the *n*-hexane solution was further investigated with polarized optical microscopy. As expected for stiff rod-like aggregates, the solution (8 wt%) shows to be highly birefringent with a thread-like texture on polarized optical microscopy indicative of the formation of a lyotropic nematic liquid crystal.



**Figure 2.** (a) TEM image of the nanofibers of **1** in aqueous solution, (b) cross-section TEM image of the nanofibers of **1** in aqueous solution, and (c) TEM image of the nanofibers of **1** in *n*-hexane solution, and (d) a representative optical polarized micrograph of the nematic phase in *n*-hexane solution.

### Conclusions

The notable feature of the amphiphilic wedge-coil block molecule investigated here is its ability to self-assemble into cylindrical nanofibers in both polar as well as nonpolar solvents. Remarkably, the resulting nanofibers, as solvent polarity change from water to *n*-hexane, change from highly flexible coil-like to stiff rod-like characteristics. This switching in the stiffness of the nanofibers in response to solvent polarity is attributed to the structural inversion of cylindrical core from bulky dendritic segments with amorphous nature to crystallizable linear PEO segments. This dynamic structural variation depending on the solvent environment may find useful applications in many areas including development of intelligent supramolecular materials.

### References

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