

Reversible Switching between Nematic Gel and Isotropic Fluid Triggered by External Stimuli in Aqueous Self-Assembly of Supramolecular Nanocylinders

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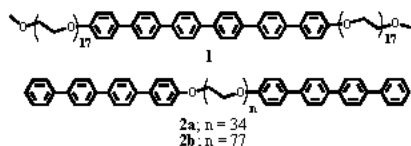
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Introduction

Spontaneous formation of supramolecular architectures by self-assembly of amphiphilic molecules is of great interest in areas ranging from chemistry, biology to materials science, driven by a wide variety of potential application. Extensive efforts thus have been directed toward functional supramolecular systems for exploration of novel properties and functions that are difficult without specific assembly of molecular components. Self-assembling molecules based on *p*-conjugated rods are receiving increased attention as building block for electro-optically active supramolecular structures, such as discrete bundles, cylinders, and vesicles. Recently, we have shown that incorporation of a conjugated rod into an amphiphilic dumbbell-shaped molecular architecture give rise to the formation of a helical nanostructure, consisting of hydrophobic aromatic cores surrounded by hydrophilic flexible segments that are exposed to the aqueous environment.

Results and discussion

We present herein the formation of discrete nanocylinders from self-assembly of a coil-rod-coil molecule (**1**) based on a conjugated rod segment in aqueous solution and reversible switching between nematic gel and isotropic fluid triggered by addition of a rod-coil-rod molecule (**2b**) in hierarchical self-assembly of supramolecular nanocylinders (Figure 1).



The coil-rod-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. **1** was observed to self-assemble into discrete spherical micelle at initial stage. However, these micelles showed to slowly change into cylindrical objects on time scale of a week, indicating that cylindrical aggregates are thermodynamically stable objects in this system. The evidence for the formation of the cylindrical aggregates was provided by transmission electron microscopy (TEM) experiments. The micrographs with negative stained samples show cylindrical aggregates with a uniform diameter of about 10 nm and lengths up to several hundreds of nanometers.

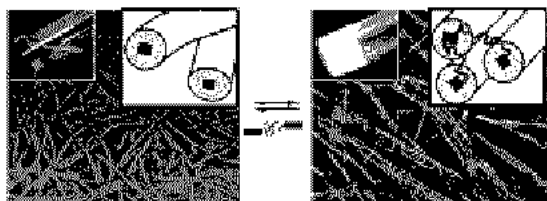


Figure 1. Reversible switching between nematic gel and isotropic fluid.

Remarkably, addition of **2b** at the concentration from 2 to 30 wt% relative to **1** induces anisotropic gelation of the isotropic fluid phase of **1**, which is considered to be the result of a dynamic cross-link of the individual cylindrical micelles by coassembly with **2b**. The polarized optical micrographs (POM) for the gels show a threadlike texture, characteristic of a nematic structure. In this region, the SAXS pattern

shows only a single broad peak at d-spacing of 14 nm, indicative of the distance between the cylinders of a nematic structure, and the wide angle X-ray scattering patterns shows the inter-rod interaction peak at $q = 14 \text{ nm}^{-1}$ and the two water peaks at 20 and 27 nm^{-1} .

TEM performed with the solution of 10 wt% **2b** relative to **1** shows bundles of fastening several strands, in contrast to flexible, individual strands of only **1** solution. Fastening the strands leads to forming of the network via physical cross-link with rod-coil-rod molecules. **2b** interconnect cylinders aligned in a parallel fashion through hydrophobic- and π - π interactions. At the fasten regions, several strands that are lying next to each other split up and continue separately to refasten some other strand later on. Fastening the strands can give rise to increase the rigidity of bundles of high aspect ratio, therefore form the nematic gel. The density profiles taken perpendicular to the long axis of the bundle conformed inter-cylinders distance to be about 14 nm.

To further investigate fastening the cylinders, the viscosities of 1 to 15 g/L aqueous solutions of **1**, **1•2a** and **1•2b** have been measured at 25 °C by means of a capillary viscosimeter. The curve exhibited clearly distinguished, as increasing the concentration, **1** and **1•2a** solutions slightly increase, while the solution of **1•2b** abruptly increases. These results indicate that **2a** is too short to interconnect the cylinders, while **2b** with much longer molecular length binds the cylinders consisting of self-assembled **1** to be more viscose.

To confirm the reversible switching between nematic gel and isotropic fluid phase according to an amount of **2b**, the gelation behavior was investigated when the total concentration of solution fixed at 3.0 wt% with the concentration of **2b** relative to **1** changing from 5 to 10 wt%, by using POM. 5 wt% **2b** solution is isotropic fluid. In this solution, adding the **2b** to 10wt% leads to the strong birefringence of nematic texture, indicating that the gelation occurs, and then to reduce weight percent of **2b**, adding **1** solution to be 5 wt% **2b** give rise to disappearance of the birefringence again. These results mean that as an amount of **2b**, the transition between nematic gel and isotropic fluid phase is reversible.

These interconnection leads to stiff bundles of several nanocylinders to be nematic gel. Notably, the gelation can be reversible via an amount of rod-coil-rod molecules. These results suggest that reversible switching between nematic gel and isotropic fluid can be triggered by external stimuli in aqueous self-assembly of supramolecular nanocylinders, which potentially have a number of applications including tissue engineering and drug delivery such as biocompatible materials.

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