

Shape-Persistent Macromolecular Disks from Reactive Supramolecular Rod Bundles

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One of the important goals of contemporary science is the molecular design of nanometer-scale materials in order to achieve specific properties. Control of molecular assembly and subsequent organization of these nanoscale entities could be one way to construct these materials.¹ Rigid rod-shaped molecular architectures containing flexible chains on their ends have proven to self-assemble into a large variety of organized supramolecular structures, including discrete nanostructures.² It was reported that the formation of discrete aggregates could be possible if steric constraints are built into the rod-coil design. Increasing the coil volume fraction is one possible approach to bring about the formation of such nanostructures.³ Incorporation of flexible branched chains with a large cross-sectional area to generate rod-coil triblock molecules proved to be another efficient approach to creating discrete nanostructures.⁴ If supramolecular bundles are formed spontaneously in bulk films, by inclusion of appropriate reactive groups it should be possible to convert these into molecular objects by cross-linking, while maintaining the precise size and shape of the rod bundles. To obtain well-defined macromolecular objects from a preassembled supramolecular structure, the spatial isolation of reactive groups within each supramolecular unit is required.⁵ Thus, we synthesized a coil-rod-coil triblock molecule ($f_{\text{coil}} = 0.73$) with a reactive rod block that self-assembles into a discrete supramolecular structure (Figure 1).

In this Communication, we report the preparation of nano-objects through selective stitching of the aromatic disklike domains in the three-dimensional hexagonal close-packed structure formed by a coil-rod-coil molecule with a reactive rod block by photo-cross-linking (Figure 1). The synthesis of a polymerizable coil-rod-coil molecule consisting of five biphenyl units linked through benzyl ether linkage and poly(propylene oxide)s at its ends was performed in a stepwise fashion, starting with etherification of poly(propylene oxide) and 4,4'-biphenol, and continuing with etherification reaction with 4,4'-bis(bromomethyl)biphenyl to generate the precursor rod-coil molecule. The polymerizable coil-rod-coil molecule was synthesized by treating the precursor molecule with 2,2'-divinyl-4,4'-biphenol. The coil-rod-coil molecule containing reactive vinyl groups was characterized by ¹H and ¹³C NMR spectroscopy, elemental analysis, and gel permeation chromatography (GPC) and shown to be in full agreement with the structure presented.

Coil-rod-coil molecule **1** melts into the liquid crystalline phase at 89 °C, and then transforms into an isotropic liquid at 113 °C, as confirmed by differential scanning calorimetry (DSC) (Figure 2a). On slow cooling from the isotropic state, a spherulitic texture with arced striations was observed by optical polarized microscopy, indicative of the presence of a 3-D hexagonally ordered liquid crystalline phase.⁶ Small-angle X-ray scattering (SAXS) measurements in the melt state showed a number of well-resolved reflections, which can be indexed as a 3-D hexagonal order ($P6_3/mmc$ space group symmetry) with lattice constants $a = 9.2$ nm and $c = 15.6$ nm (Figure 2b).^{6,7} Wide-angle X-ray diffraction

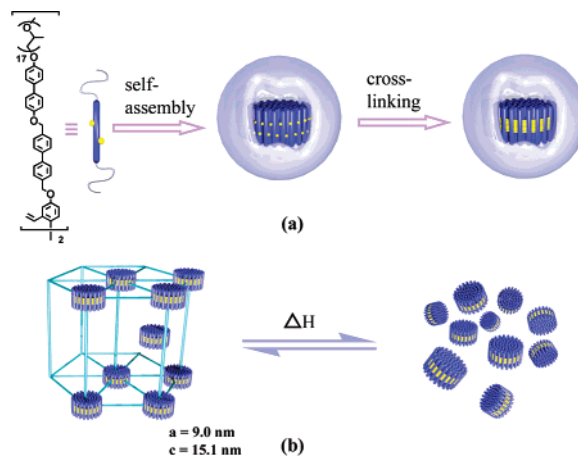


Figure 1. Schematic representation of (a) self-assembly of rod-coil monomer and subsequent conversion to macromolecular object by cross-linking, and (b) hexagonal close-packed structure of the object and its transformation into an isotropic liquid state.

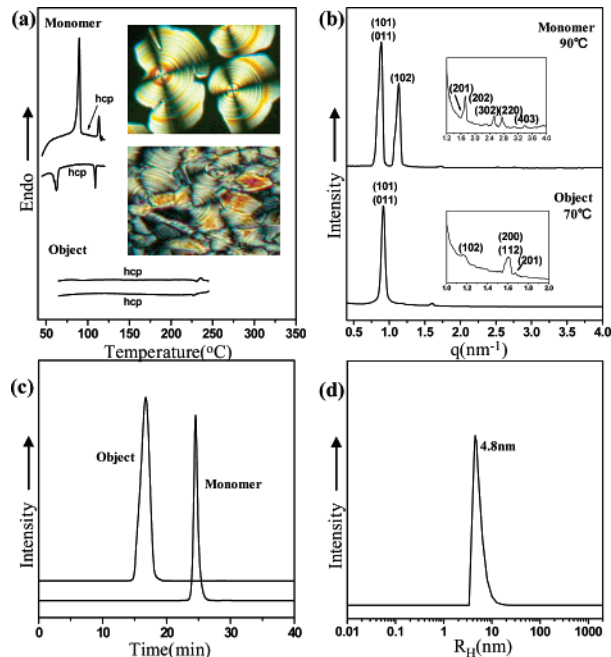


Figure 2. (a) DSC curves and optically polarized microscopic textures exhibited by monomer at 109 °C on the cooling scan (inset above) and by object at 210 °C on the cooling scan (inset below); (b) SAXS patterns; (c) GPC traces; and (d) dynamic light scattering pattern of the macromolecular object measured in chloroform solution.

patterns showed only a broad halo, indicative of a liquid crystalline order. These results, together with optical microscopic observations, indicate that **1** self-assembles into discrete rod bundles that are

encapsulated by poly(propylene oxide) coils and subsequently organize into a 3-D hexagonal close-packed structure in the melt state.

Cross-linking under UV irradiation with 254 nm of **1** in a liquid crystalline phase at 93 °C under nitrogen atmosphere for several hours resulted in the formation of a completely soluble macromolecule.⁸ After cross-linking, the thermal stability of the 3-D structure appeared to increase significantly, as shown in Figure 2a. GPC traces showed that the molecular weight appeared to be 270 kDa, with a narrow molecular weight distribution ($M_w/M_n = 1.08$) after polymerization (Figure 2c). ¹H NMR spectra taken from the chloroform solutions showed the complete disappearance of the resonances associated with vinyl groups after polymerization. Small-angle X-ray scattering revealed several reflections corresponding to a 3-D hexagonal lattice with essentially the same lattice constants ($a = 9.0$ nm, $c = 15.1$ nm) as those of the coil-rod-coil molecule (Figure 2b), indicative of the preservation of the ordered symmetry and the dimensions of the discrete objects after polymerization. On the basis of these lattice constants and measured density, the number of constituent units in each object was estimated to be approximately 112. The molecular objects would then have a molar mass of approximately 330 kDa, which is higher than that determined from GPC. An underestimated molecular weight by GPC can be attributed to a significantly more compact globular shape of the molecular objects compared to that of linear polystyrene chains of the same molecular weight. Considering that the long axes of the rod-building blocks are aligned parallel to each other, the covalently binding of 112 rod segments in a polymerized object can be estimated to generate a macromolecular aromatic core with a disklike object 6.1 nm in diameter and 5.0 nm in length (estimated from CPK model). On the basis of the results described above, it can be concluded that polymerization proceeds with retention of the size and shape of the self-assembled rod bundles, giving rise to the formation of macromolecular disklike objects with well-defined shape and size.

Remarkably, DSC indicated that the macromolecular objects exhibit reversible first-order transitions on both heating and cooling scans (Figure 2a), implying that these disk-shaped objects are stable in the isotropic state.⁹ This behavior of the objects was also confirmed by optical polarized microscopy. On slow cooling from the isotropic state, platelet-like domains with striations that merge into an arced pseudo-focal conic domain were observed, indicative of the presence of a hexagonal structure.⁶ The macromolecular objects were also readily soluble in common organic solvents such as THF, CH₂Cl₂, CHCl₃, and ethyl acetate, and their isolation from the solutions reversibly recovered an ordered structure, as evidenced by optical polarized microscopic observations. This observation suggests that the macromolecular objects are stable in shape even in the isotropic solution, which is further supported by dynamic light scatterings (DLS). DLS measurements for chloroform solutions showed that the average hydrodynamic radius (R_H) of the nano-objects was 4.8 nm with a narrow size distribution (Figure 2d), suggesting that the objects consist of a shape-persistent disklike aromatic core encapsulated by flexible poly(propylene oxide) coils. The slightly larger diameter obtained by DLS compared to that determined from SAXS can be attributed to swelling of coil segments.

In summary, we have developed a polymerizable coil-rod-coil molecule that self-organizes into a 3-D hexagonal close-packed discrete structure in the melt state. Cross-linking in the 3-D ordered state proceeded with the retention of the ordered structure, leading to the formation of macromolecular objects with well-defined shape and size. The 3-D hexagonal close-packed structure was observed to recover after isolation from the solutions and transform into an isotropic liquid in the bulk state in a reversible way, suggesting that the macromolecular objects are shape-persistent in solutions as well as an isotropic liquid phase of the bulk. The polymerization of reactive rod blocks within the confined space described here offers a novel strategy to create shape-persistent nano-objects which potentially have applications as diverse as giant dendrimers, macromolecular reactors, and hybrid nanomaterials.

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Supporting Information Available: Detailed synthetic procedures, characterization, and thermal analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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