

# Functionalized supramolecular materials

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The design and creation of regularly shaped nanoscale objects which can serve as building blocks of supramolecular materials is an extremely important goal in materials science. Controlling the spatial organization of such objects could deliver materials with defined chemical and topographical nanoscale features, potentially leading to novel physical properties or integrating several properties in a single material. Herein, we report on a class of triblock rodcoil molecules that self organize into supramolecular units of regular shape and size. The materials formed by these supramolecular units are characterized by small angle X-ray scattering, transmission electron microscopy, second harmonic generation, and photoluminescence. Interestingly, second harmonic generation indicates the packing of supramolecular units is polar within self-organized films with thicknesses on the order of microns. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

A remaining challenge in synthetic chemistry is the ability to design and create specific supramolecular nanostructures of diverse shape and function. This ability would be of great benefit to materials science, as it would provide new units from which materials could be constructed. These new units would resemble folded proteins, in that they could be made shape invariant, with designed chemical functionality at specific locations on the structure. Such units could be assembled into designer networks, 2D and 3D superlattices, solids with well-defined nanopores, chemically and topographically defined surfaces, and uniquely packed assemblies. Adding specific chemical functionalities to surface sectors of these units could lead to coordination chemistry on a large scale, connecting nanostructures rather than ions with small molecules. Since it is not currently feasible to create these structures as individual covalent chemical compounds, we look to the self assembly of small molecules into supramolecular polymers which would be roughly the size of folded proteins and polymers in solution. To date, research in supramolecular chemistry, pioneered by Lehn and coworkers<sup>1</sup>, has focused on small aggregates of molecules<sup>2,3</sup>, 1D chains of irregular length<sup>1</sup>, attachment of side chains to polydisperse linear polymers<sup>4,5</sup>, and small dendrimers<sup>6</sup>. The development of new molecules for self assembly, and the understanding of the thermodynamic rules governing the formation of large supramolecular nanostructures remain important scientific goals. This work describes a family of self-assembling molecules that form supramolecular materials with highly regular nanostructures. Previous work with the molecules described here was reported elsewhere<sup>7</sup>.

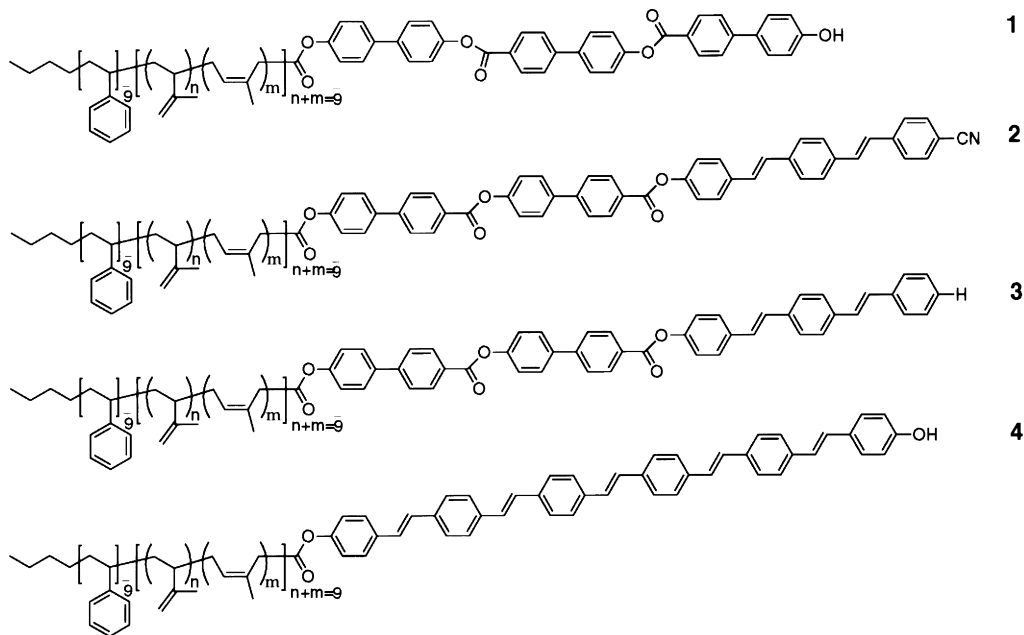
## MUSHROOM-SHAPED NANOSTRUCTURES FROM TRIBLOCK MOLECULES

Construction of the triblock molecules was inspired by the architecture of block copolymers. The original triblock molecule was composed of short styrene and isoprene blocks connected to several aromatic biphenyl units, comprising a molecule described as a rodcoil, with two flexible segments and one stiff segment. The oligostyrene and oligoisoprene blocks were synthesized using living anionic polymerization. The average degree of polymerization for both was 9, with a polydispersity index of 1.06–1.10. Biphenyl unit segments of the rod are then sequentially attached to the carboxyl-terminated diblock coil, forming the triblock rodcoil molecule. This methodology affords a collection of molecules with polydisperse coil segments, but perfectly monodisperse rod segments. Attachment of three biphenyl units results in **1** shown in *Figure 1*.

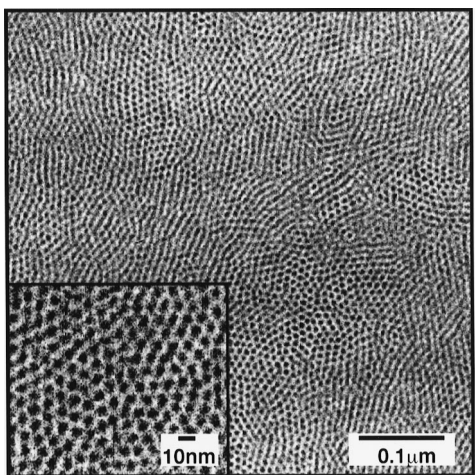
Transmission electron microscopy (TEM) examination of these rodcoil molecules shows they self organize into well-defined nanoaggregates when cast from solution. *Figure 2* is an unstained electron micrograph revealing the regularity in both size and shape of the nanoaggregates. Electron microscopy and diffraction of these aggregates indicate they are composed of approximately 100 molecules. Until now, the preparation of well-defined supramolecular units with molar masses in the hundreds of kDa had not been reported.

Small angle X-ray scattering (SAXS) studies indicate that the supramolecular units of **1** stack into layers with a d-spacing of 74 Å. The length of **1** in its fully extended conformation is ~100 Å, suggesting monolayer formation<sup>8</sup>. A series of ultramicrotomy experiments were performed in order to more fully investigate monolayer formation in this system. TEM micrographs of these ultramicrotomed samples,

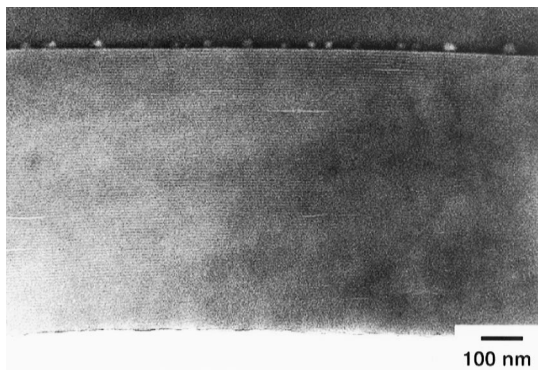
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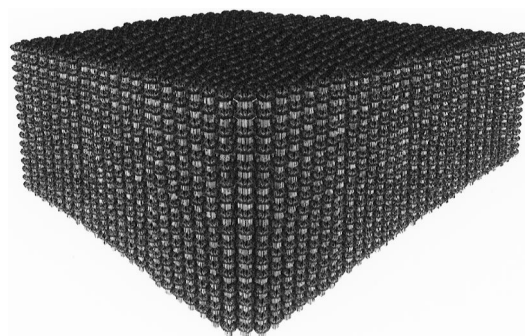
**Figure 1** Chemical structure of four triblock rodcoil molecules having average degree of polymerization of 9 for styrene and isoprene



**Figure 2** TEM micrograph of the supramolecular film of **1**, the contrast arises from both diffraction and phase contrast. The dark regions are attributed to the crystalline rod domains while the lighter regions are assigned to the amorphous coil segments. The micrograph clearly shows the superlattice formed by these nanostructures



**Figure 3** TEM micrograph of an ultramicrotomed cross-section of a film of **1** shows the material is organized into layers



**Figure 4** A schematic representation of how the mushroom-shaped nanostructures stack in 'cap to stem' polar fashion

shown in *Figure 3*, reveal the formation of large domains of oriented stripes over a thickness of one micron. The dark bands are interpreted as containing the rigid molecular segments, while the light bands are presumed to contain the flexible molecular segments. The presence of bands indicates that the aggregates comprising the monolayer are uniformly aligned, as shown in *Figure 4*.

In order to establish the polar nature of these supramolecular films, second-order nonlinear optical activity experiments were performed. The films, as envisioned in *Figure 4*, would not possess a center of inversion, and would result in the generation of a second harmonic (SHG) signal from the material. SHG measurements on films of **1** confirm the polar nature of this material<sup>7</sup>. This is of interest since the formation of polar ordered materials has many implications in materials technology. These include piezoelectricity, pyroelectricity, materials coupling for composites since they could adhere to two different materials on opposite surfaces, second-order nonlinear optical activity, and adhesive coatings with protective functions because tape-like character could be induced by the polar structure.

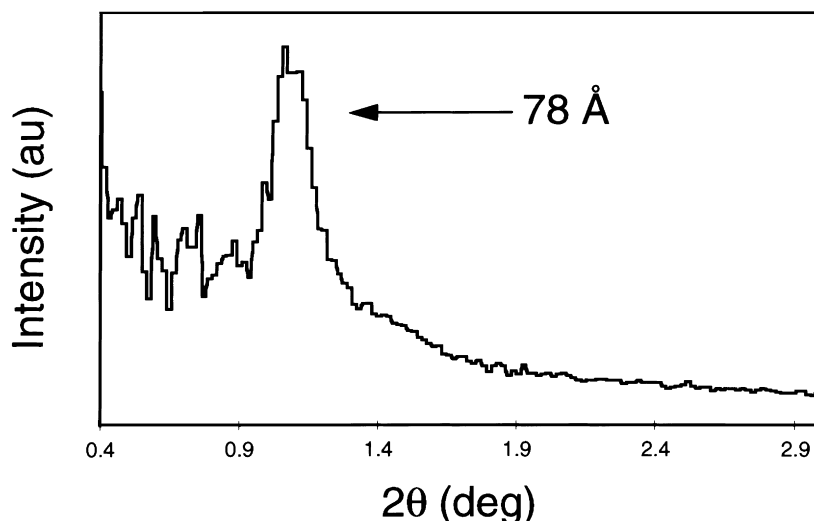


Figure 5 SAXS scans of **2** revealing monolayer spacings of 78 Å for annealed films

### PHOTOLUMINESCENT NANOSTRUCTURES

The triblock rodcoil motif allows multiple sites for functionality to be designed into the system to create novel supramolecular materials. A phenylene vinylene segment has been integrated into the rod portion of the triblock molecule to create luminescent supramolecular objects. For our system, phenylene vinylene represents an ideal choice because the molecular segment is rigid in addition to being a robust material with interesting electronic properties. Two biphenyl segments were attached to the same sequence of carboxylated oligo(styrene-co-isoprene) used to synthesize **1**. After attaching the biphenyl segments, the phenylene vinylene rod blocks were connected using standard esterification chemistry. The phenylene vinylene segments were prepared by Horner–Emmons olefination chemistry which affords high yields of the *E*-isomer<sup>9</sup>. The rodcoil molecules, **2** and **3**, in Figure 1 are similar in chemical structure; however, **2** contains a cyano terminus while **3** possesses a hydrogen terminus. In addition, Figure 1 shows we have prepared rodcoil molecules, **4**, which contain only phenylene vinylene rod segments.

Molecules **2**, **3**, and **4** were characterized by polarized optical microscopy and SAXS. The molecules exhibit thermotropic liquid crystalline behavior over broad temperature ranges (>150°C). The textures resemble smectic phases or layered structures which is confirmed by SAXS. SAXS measurements suggest these molecules form films composed of monolayer structures of the type required for polar order. Annealed films of **2** exhibit (001) reflections corresponding to d-spacings of 78 Å as shown in Figure 5, while **3** and **4** each show one reflection corresponding to d-spacings of 76 Å and 85 Å, respectively. Dilute solutions and, perhaps more interestingly, solid films of these materials show strong photoluminescence. The photoluminescence spectra of dilute solutions of **2** and **3** show emissions at 450 nm and 420 nm, respectively, when excited with 331 nm light. It is possible that the strong solid state photoluminescence is linked to the nanostructured nature of these materials. Furthermore, preliminary results suggest these films are polar, illustrating the principle of property integration in supramolecular materials<sup>10</sup>.

### MECHANISM FOR SUPRAMOLECULAR UNIT FORMATION

The triblock rodcoil molecule is programmed to frustrate the formation of infinite layers through the incorporation of a unit which creates steric, repulsive forces on a molecule also containing a mesogenic segment capable of parallel packing. The aim of the work was to create materials in which molecular layers self-partition into nanoscale objects. The oligo(styrene-co-isoprene) diblock segment contains a great deal of chemical aperiodicity; the styrene block is an atactic sequence of meso and racemic diads while the isoprene block is composed of primarily 1,4 and 3,4 additions with some 1,2 repeat units as well. This high degree of chemical diversity is believed to be essential to the novel and interesting structures formed by rodcoil molecules because it frustrates three-dimensional crystallization. Separated from each other, the coil portion of the molecule would assume a random coil-type conformation in solution, while the rod block would aggregate due to its tendency toward  $\pi$ - $\pi$  stacking. The presence of a covalently connected coil limits the aggregation of the rod blocks, and leads to the formation of nanoscale objects. In order for the rod blocks to crystallize, the coil blocks must be excluded from the crystalline phase. Furthermore, as crystallization proceeds, the styrene blocks will experience increasing hard-core repulsive forces due to their larger cross-sectional area, limiting the aggregate size. We believe it is the balance between the attractive forces of rod segments and the repulsive interactions between coil segments which leads to the formation of well-defined supramolecular units. However, the entropic penalties associated with the formation of these aggregates need to be considered. Aside from the normal entropic cost of aggregation, the coils must become stretched in order for the molecules to aggregate. This stretching of the coils creates an entropic penalty, further increasing the free energy cost in the formation of large aggregates.

Several computer simulations were performed to investigate possible modes of rod aggregation. A tightly packed bundle of 13 rod segments was created in the molecular modeling package SYBYL<sup>8</sup>, and then allowed to relax via conjugate gradient minimization. Once the cluster was fully relaxed, the energy of the cluster was calculated using the

Tripos force field. Two specific clusters were examined: one with all the rods aligned in the same direction, and a second with half the rods aligned antiparallel to those remaining. These clusters are termed ferro and antiferro, respectively, and several clusters of each type were built and evaluated. The ferro rod clusters had an average energy of  $-273$  kcal/mol, while the average energy of the antiferro rod clusters was  $-223$  kcal/mol, indicating a preference for the rods to form ferro clusters. Next, clusters of 13 coil segments were built and evaluated in the same manner as the rods. The relaxed coil clusters had energies of 34.4 kcal/mol and 74.4 kcal/mol for the ferro and antiferro cases, respectively. If the relaxed clusters are examined in a plane perpendicular to the average molecular axis, one can measure the average cross-sectional area of a molecule in the cluster. In the ferro rod cluster, the average molecule occupies  $16 \text{ \AA}^2$  while in the ferro coil cluster, the average molecule occupies  $33 \text{ \AA}^2$ . The coils clearly do not pack as favorably, or as densely as the rods are able to. These simulations indicate that the hard core repulsions between coils could frustrate long range crystallization of the rod segments, leading to the formation of finite supramolecular units.

## CONCLUSIONS

We report here on triblock rodcoil molecules that spontaneously organize into regular nanostructures resulting in macroscopically organized materials. All supramolecular materials discussed have bulk polar order as characterized by SAXS and second-order NLO studies. We propose that supramolecular unit formation arises from the balance between attractive forces among rod segments and repulsive forces between coil segments of the triblock rodcoil

molecules. Preliminary computer simulations are presented in support of this mechanism.

## ACKNOWLEDGMENTS

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