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Supramolecular Self-Assembly of Three-Dimensional Nanostructures and Microstructures: Microcapsules from Electroactive and Photoactive Rod−Coil−Rod Triblock Copolymers

X. Linda Chen and Samson A. Jenekhe*

Department of Chemical Engineering, University of Rochester, Rochester, New York 14627-0166

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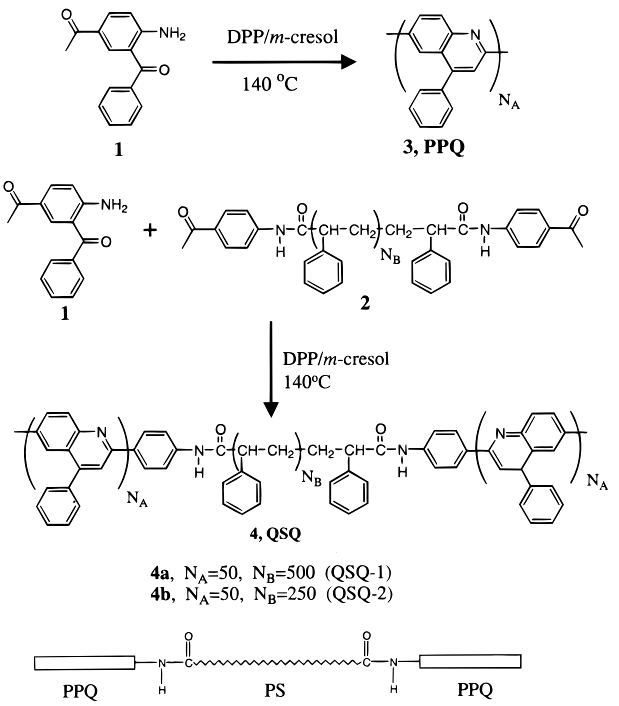
The synthesis and use of suitable block copolymers as building blocks for the self-organization of functional supramolecular nanostructures and microstructures can also be considered a major part of the emerging field of *supramolecular polymer chemistry*.[1,2] Rod−coil or rigid−flexible block copolymers[2−6] in particular offer opportunities for engineering novel features, functions and properties into supramolecular polymer assemblies through the rodlike component. For example, rod−coil block copolymers containing π-conjugated polymer blocks have been found to have optoelectronic properties that varied with the supramolecular morphology.[3] One of the fundamental goals of this field should, thus, be the understanding of the relationships of macromolecular architecture to the self-assembly processes and to the morphology and novel properties of supramolecular polymer assemblies.

So far, the rod (A)−coil (B) block copolymer architectures that have been investigated include AB rod−coil diblocks and BAB *coil−rod−coil* triblocks.[2−6] The ABA *rod−coil−rod* triblock architecture which is yet to be investigated is of special interest because of its potential to form stable *folded* or *hairpin* conformations unlike the AB diblock and BAB triblock. Similar to known *coil−coil−coil* triblock copolymers,[7] we expect such an *intramolecular folding* to exert important influence on the self-assembly of ABA rod−coil−rod triblock copolymers.

In this communication, we report the synthesis and supramolecular self-assembly of a novel rod (A)−coil (B)−rod (A) triblock copolymer architecture with the general structure A−NHCO−B−CONH−A. The new quinoline−styrene−quinoline (QSQ) triblock copolymers (Scheme 1) were found to spontaneously form robust microcapsules or spherical vesicles in solution. Because the π-conjugated rigid rod poly(phenylquinoline) (PPQ) incorporated into QSQ triblock copolymers has known electronic, optoelectronic, and photonic properties,[8] these electroactive and photoactive microcapsules are among the first supramolecular assemblies endowed with such properties of conjugated polymers.[3] Polarized optical, fluorescence optical, and scanning electron microscopies were used to reveal the supramolecular morphology.

Synthesis and Characterization. Optimized polymerization conditions for the synthesis[9] of the PPQ homopolymer (**3**) were adapted for the preparation of the rod−coil−rod triblock copolymers in diphenyl phosphate (DPP)/*m*-cresol (Scheme 1). Copolymerization of 5-acetyl-2-aminobenzophenone (**1**) with diacetyl functionalized[3a] low polydispersity ($M_w/M_n = 1.05$) polystyrene (**2**) gave the QSQ (**4**) triblock copolymers. Repeated Soxhlet extractions with refluxing ethyl acetate which is a good solvent for polystyrene (PS) homopolymer or **2** ensured the absence of PS homopolymer contamination. Complete insolubility of the triblock copolymers **4** in formic acid, which is an excellent solvent for the PPQ homopolymer, confirmed the absence of contamination from this homopolymer. The average degree of polymerization of the PPQ block and, hence, the composition of the QSQ triblocks were controlled by the reaction stoichiometry and subsequently confirmed by ^{1}H NMR spectra and thermogravimetric analysis (TGA). FTIR spectra also confirmed the structure of the block copolymers.

Scheme 1



^{1}H NMR spectra (not shown) of **4a**−**4b** in deuterated nitrobenzene containing gallium trichloride ($C_6H_5NO_2$/$GaCl_3$)[10] were obtained and assigned to the proposed structures by comparison with the spectra of PPQ and PS homopolymers. By comparison of the integrated proton resonances in the 8.8−8.9 ppm range which are unique to the PPQ block to those at 1.5−2.2 ppm (CH_2 units of PS) we determined the average repeat units of each of the two PPQ blocks (N_A) in **4a** and **4b** to be 49 and 50, respectively. These results compare favorably to $N_A = 50$ calculated from the reaction stoichiometry of 100% yield which was observed in the copolymerizations. The measured weight loss in the 400−600 °C range in TGA experiments were 70 and 51%, respectively, for **4a** and **4b**. From these TGA data we also estimated N_A to be 50 and 52 for **4a** and **4b**, respectively. Although the polydispersity of the PPQ blocks is not known, we expect it to be on the order of 1.5−2.0 based on related homopolyquinolines[9] and the theoretically expected value for high conversion condensation polymerization. Differential scanning calorimetry (DSC) of the copolymers showed that they did not exhibit thermotropic mesophases. Both QSQ-1 (**4a)** and QSQ-2 (**4b**) copolymers had a T_g of 114 °C, which is slightly

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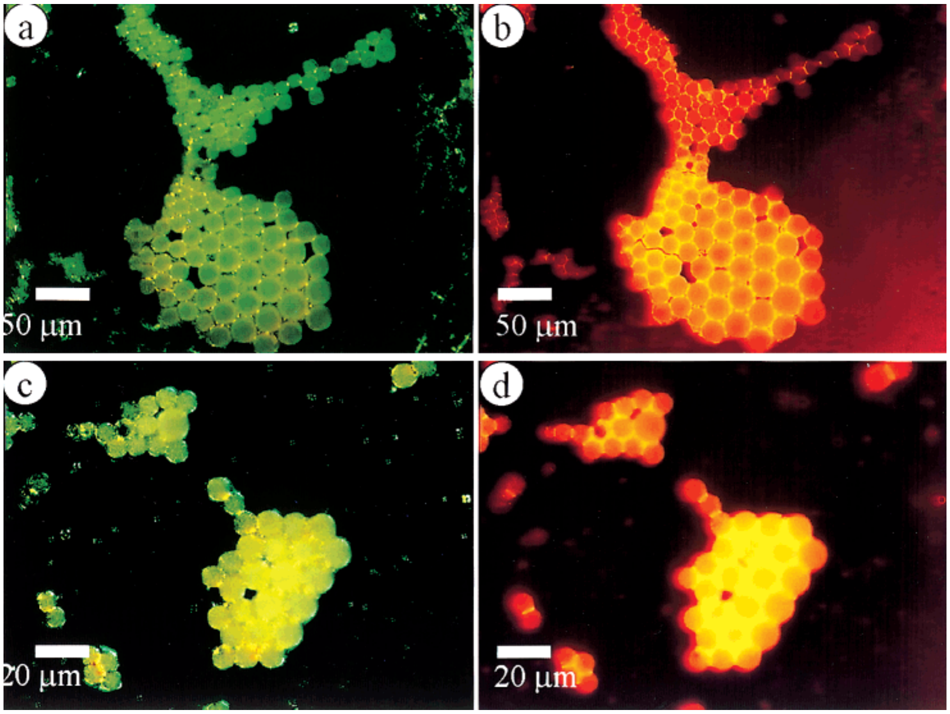

Figure 1. Polarized optical and fluorescence micrographs of solid microcapsules dried from QSQ-1 (a,b) and QSQ-2 (c,d) triblock copolymer dispersions. Images a and c were taken under cross-polarizers and the rest are fluorescence (540 nm excitation) images.

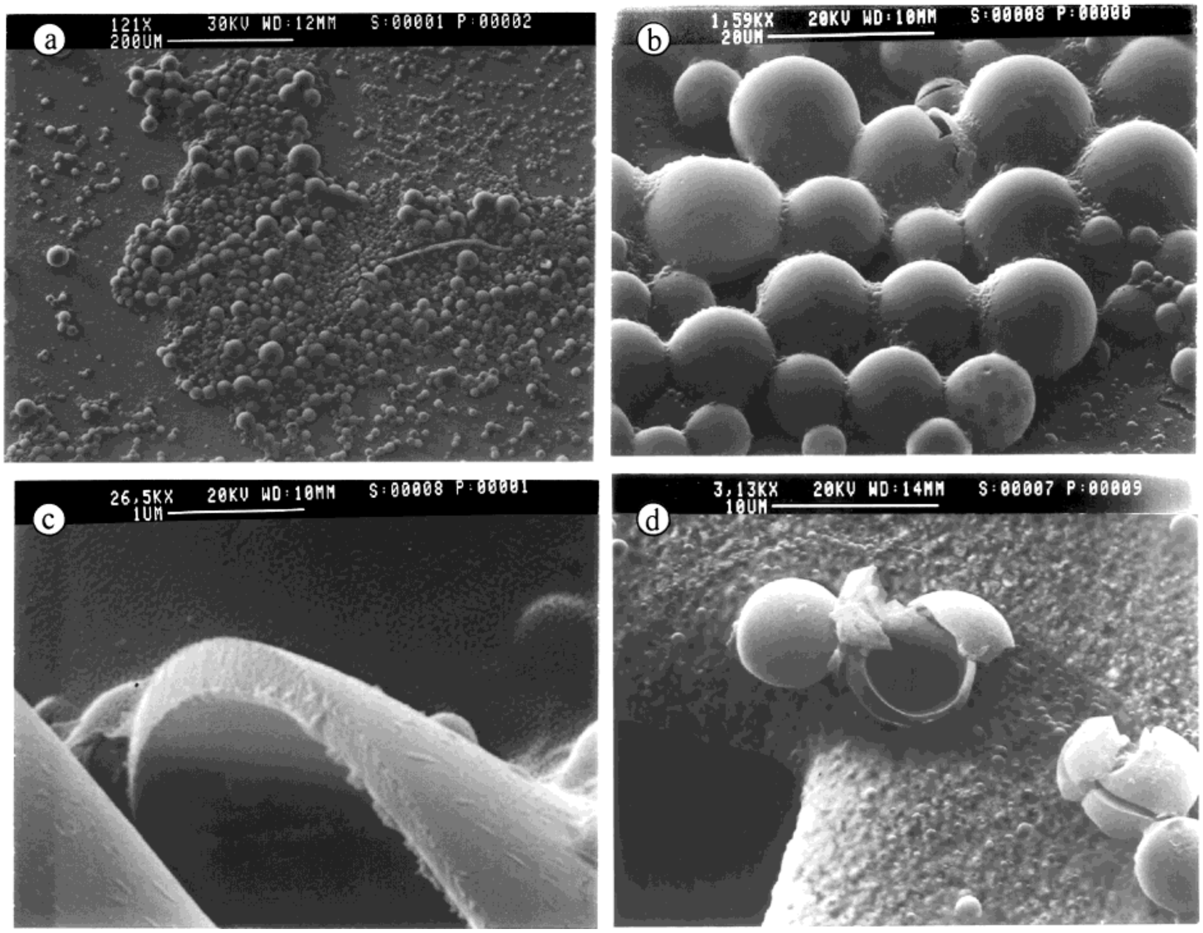

Figure 2. SEM images of microcapsules from QSQ-2 copolymer solutions dried at 25 °C and coated with 10 nm gold layer. The broken microcapsule in part b is magnified in part c.

enhanced compared to PS homopolymer (100 °C).

Self-Assembly and Supramolecular Morphology. Upon dissolving either QSQ-1 or QSQ-2 copolymer sample in a mixed solvent (trifluoroacetic acid: dichloromethane, TFA:DCM of various ratios) at room temperature (25 °C), without sonication, mechanical stirring or other form of applied energy, microcapsules or spherical vesicles formed spontaneously from the dilute solutions (0.01−0.5 wt %). Polarized optical and fluorescence microscopies were used to visualize the supramolecular assemblies of the triblock copolymers after drying solutions on a glass slide (Figure 1). The diameter of the microcapsules was in the range 1−200 μm depending on the triblock composition and solution concentration. The size distribution of microcapsules of QSQ-1 was about 80% in the 20−40 μm range (Figure 1a,b), 10% in the 1−5 μm range, and 10% in the 50−200 μm range; the typical QSQ-1 microcapsule had a diameter of ~27 μm. Microcapsules of QSQ-2 were less polydisperse with ~90% having diameters in the 10−20 μm range (Figure 1c,d) with the remaining ones in the 1−5 μm range. The average size of the QSQ-2 vesicles was 16 μm. The results of our extensive investigation of the possible effects of solution drying temperature (20−95 °C), concentration (0.01−0.5 wt %), and solvent ratio (TFA:DCM = 9/1 to 1/9) on the supramolecular morphology of the microcapsules, showed no effect of these variables on *size* and *shape*. However, microcapsules were not observed by optical microscopy of any triblock copolymer solution at 0.001 wt %, which indicates either a critical concentration for macrocapsule assembly or the presence of aggregates with sizes below the resolution of optical microscopy.

It is interesting that only *spherical microcapsules (or vesicles)* were formed from QSQ triblock copolymers under all the self-assembly conditions tried. This contrasts sharply from the multiple morphologies observed in the self-organized aggregates of the related rod−coil *diblock* copolymers, A−NHCO−B,[3a] or the coil−rod−coil B−CONH−A−NHCO−B triblocks, which form only smectic liquid crystals.[6] This implies that spherical vesicles are the thermodynamically more stable aggregates of the *triblock* copolymers compared to the flat disks, microtubules, or other morphologies.[3a] Another interesting feature of these triblock copolymer microcapsules is their propensity for self-organization into higher order microstructures (Figure 1). Highly ordered, close-packed hexagonal arrays of the microcapsules were commonly observed in the QSQ-1 and QSQ-2 samples. Although some elastic deformation at the area of contact is commonly observed in soft colloidal particles or phospholipid vesicles that aggregate,[11] it is at a minimum in these block copolymer microcapsules. It has been suggested that higher order assemblies of hollow spheres or vesicles, such as observed here, could be used to prepare photonic crystals[3b] or as simple models of biological tissue.[11]

Visualization of the QSQ microcapsules by scanning electron microscopy (SEM) confirmed the sizes and 3-D shape seen in optical microscopy and provided new information about the hollow cavity, wall thickness, and the small-diameter (<1 μm) microcapsules (Figure 2). Dimples or partial flattening of the largest (~100−200 μm) vesicles were observed only with QSQ-1. If the ca. 10 nm gold layer thickness is taken into account a wall thickness of about 360 nm is estimated from Figure 2c, which means about three molecular layers of the approximately 120 nm chains of QSQ-2. The wall thicknesses estimated from SEM for all the QSQ microcapsules were in the range 250−1200 nm which indicates that they are multilayered shells. About 5−10% of the QSQ-1 and QSQ-2 assemblies observed in the SEM had diameters in the 200−800 nm range. These results suggest that the folded conformations of QSQ-1 and QSQ-2 are the building blocks for the self-assembly of at least the small-diameter (<800 nm) microcapsules. Additional studies by X-ray diffraction methods will be essential to achieving a detailed understanding of the supramolecular structures of the microcapsule walls.

Observation of spherical vesicles from an amphiphilic multiblock copolymer containing poly(methylphenylsilylene) and poly(ethylene oxide) sequences has also been reported.[12a] Aggregates of unknown morphology were recently revealed by neutron scattering of a poly(1,4-phenylene)-polystyrene-poly(1,4-phenylene) triblock copolymer.[12b]

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Supporting Information Available: Text giving synthetic procedures and characterization of **2**, **4a**, and **4b**, figures showing ^{1}H NMR and FTIR spectra of **4a** and TGA and DSC scans of **4a** and **4b**, and a table of ^{1}H NMR proton resonances, T_g, and TGA data for PPQ, PS, **4a**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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