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Kenneth J. Wynne
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6. AUTHOR(S)
S. A. Jenekhe and X. L. Chen

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)
University of Rochester
Department of Chemical Engineering
206 Gavett hall, Box 270166
Rochester. NY 14627-0166

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13. ABSTRACT *(Maximum 200 words)*

Block copolymer architectures containing both rigid-rod and flexible-coil blocks have novel self-organizing features and functional properties not possible with coil-coil architectures. We describe the self-assembly of new rod-coil diblock, rod-coil-rod triblock, and coil-rod-coil triblock copolymers from solution and the resulting discrete and periodic mesostructures with sizes in the 100 nanometer to 200 micrometer range. For example, hollow microspheres, cylindrical microtubules, disc-like lamellae, and doughnut shaped discrete objects self-organized from polyquinoline-b-polystyrene diblocks in a selective solvent for the polyquinoline[1a]. However, the same rod-coil diblock copolymers in a selective solvent for the polystyrene form hollow spheres which self-order into periodic mesoporous materials[1b]. The roles of macromolecular architecture and competing intermolecular interactions on the self-organized mesostructures will be shown.[1](a) Jenekhe, S. A.; Chen, X. L. Science 1998, 279, 1903-1907; (b) Science 1999, 283, 372-375.

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S. A. Jenekhe and X. L. Chen
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SELF-ASSEMBLY OF ROD-COIL BLOCK COPOLYMERS

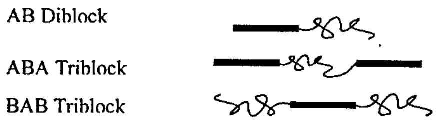
Samson A. Jenekhe and X. Linda Chen*

Departments of Chemical Engineering and Chemistry
University of Rochester, Rochester, NY 14627-0166

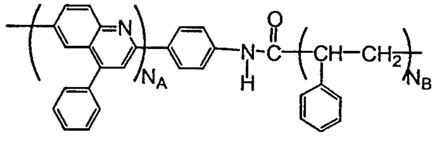
Introduction

Block copolymer architectures containing both rigid-rod and flexible-coil blocks (chart 1) can have novel self-organizing features and functional properties not possible with all-coil architectures.[1-4] The anisotropic molecular shape and stiff rodlike conformation of the rod block imparts orientational self-ordering (mesophase formation), chain stiffness, and interactional asymmetry between the blocks of rod-coil block copolymers. The expected competing interactions in such multicomponent polymer systems could be a basis for achieving self-organization over many length scales from the nanometer level to the macroscopic.[3] Although some theoretical studies of rod-coil block copolymers have been reported,[4] the level of theoretical and experimental understanding of their phase behavior, self-assembly, and self-organized mesostructures is still very rudimentary compared to coil-coil systems. Most of the experimental rod-coil block copolymers investigated to date have been those containing helical rods.[5]

Chart 1



We describe the self-assembly of new rod-coil block copolymers from solution, including AB rod-coil diblocks, ABA rod-coil-rod triblocks, and coil-rod-coil triblocks (Chart 1), and the resulting discrete and periodic mesostructures. A specific example is poly(phenylquinoline)-*block*-polystyrene (PPQ-b-PS,1) whose molecular structure is shown below. Our initial results on the self-assembly of **1** from a selective solvent for the PPQ block have been reported.[1] The unusual hierarchical self-assembly of periodic microporous materials from **1** in a selective solvent for PS has also been reported.[2] We have found that discrete mesoscopic (100 nm to 200 μm) objects such as hollow spheres, cylindrical tubules, disc-like lamellae, and doughnuts self-organized from **1** and PPQ-b-PS-b-PPQ triblock (**2**). Interestingly, **1** was able to solubilize and encapsulate large quantities of fullerenes C_{60} and C_{70}.[1,7] By employing conjugated rodlike blocks such as PPQ, which is well-known to have electronic, optoelectronic, and photonic properties, such as electrical conductivity when doped,[8] electroluminescence,[9] third order nonlinear optical effects, [10] electrochemical redox activity,[11] and photoconductivity,[12] we hope to build various functionalities into supramolecular assemblies of rod-coil block copolymers. Novel cooperative or collective properties not found in the component conjugated polymers are also anticipated in such electroactive and photoactive supramolecular assemblies of rod-coil block copolymers. Also of fundamental interest to the emerging field of *supramolecular polymer science* is that the electroactive and photoactive building blocks facilitate new ways of characterizing the self-assembly, molecular packing, aggregate morphology, and dynamics of macromolecular self-assembling mesostructures by optical and photoelectronic techniques.[1,2,6,7.]



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Experiments

The synthesis, purification, and structural characterization of all the rod-coil block copolymers are described elsewhere.[1,6] Among compositions of diblocks **1** whose self-assembling properties are described here are 50-b-300 (**1a**), 10-b-300 (**1b**), 10-b-1000 (**1c**) and 50-b-2000 (**1d**). Samples of the rod-coil-rod triblock **2** include 50-b-500-b-50 (**2a**), 50-b-250-b-50 (**2b**), and 50-b-120-b-50 (**2c**). Analytical grade solvents trifluoroacetic acid (TFA), dichloromethane (DCM), toluene, and carbon disulfide (CS_2) from Aldrich were used as received. Fullerenes C_{60} (TCI, 99.9 %) and C_{70} (Aldrich, 99 %) were used as received. Various volume ratios (e.g. 4/1, 2/1, 1/1, 1/4) of TFA/DCM or TFA/toluene binary mixtures were found to be excellent selective solvents for the rodlike PPQ block. CS_2 was a selective solvent for the PS block in the diblocks **1**. Solutions of diblock or triblock copolymer in TFA/DCM or TFA/toluene had concentrations in the range of 0.01 to 0.5 wt % (ca. 0.07 to 3.5 mg/mL)

Self-assembled aggregates of rod-coil block copolymers were dried on a substrate in air at various temperatures (20 to 90 °C) and examined by optical, fluorescence, and electron microscopies and by optical absorption and photoluminescence (PL) spectroscopies.

Results and Discussion

Some of the typical self-assembled aggregates of rod-coil diblock copolymer **1a** from a rodlike block selective solvent (TFA/dichloromethane) are shown in Figure 1. Multiple morphologies including spheres, disc-like lamellae, and cylinders were observed as the self-organization temperature and solvent composition were varied. The polymorphism of the micelle-like aggregates obtained from diblocks **1** under different conditions (solvent composition, temperature) suggests that competition among the significant intermolecular interactions (solvophobic, screened electrostatic, van der Waals, and hydrogen bonding) is a key feature in the self-assembly process of the present rod-coil block copolymers. Two remarkable features of these micellar aggregates are their robustness and sizes. For example, the aggregates were repeatedly heated to 200 °C which is above the glass transition (T_g) of PS blocks (~100 °C) but less than that of PPQ blocks (>350 °C) without deassociation or change in aggregate morphology.[1,6] The size scale of the self-organized discrete objects from diblocks **1** is up to 10-100 μm, making them comparable to self-assembled mesostructures in cellular biology.

Dissolution of triblocks **2** in TFA/DCM mixtures of various ratios (TFA/DCM = 9/1 to 1/9) at room temperature (25 °C), without sonication or other forms of applied energy, resulted in the spontaneous self-assembly of vesicles (hollow spheres) exemplified in Figure 2. Only *spherical vesicles* of various sizes were self-organized from all the rod-coil-rod triblock copolymers **2** and the different conditions (solvent composition, concentration, and temperature) investigated. This result is in sharp contrast to the multiple morphologies of aggregates self-organized from the related diblock copolymers **1**. This demonstrates the control of the three-dimensional (3-D) shape of molecular assemblies through macromolecular architecture. The diameter of vesicles of **2** was in the range of 100 nm to 200 μm; the average diameter decreased with decreasing molecular weight of the PS blocks.

We have found that whereas fullerenes C_{60} and C_{70} are insoluble in pure TFA, or TFA/DCM or TFA/toluene, they readily dissolved in the mixed protic solvents containing a diblock **1** at room temperature (25 °C). Extensive studies of the solubilization and encapsulation of fullerenes by these rod-coil diblock copolymers have shown that fullerene solubilization in DCM and toluene is enhanced by factors of 60 to 1000, the aggregation number is increased to over 10^9 chains/aggregate, and up to 10^7 to 10^{10} fullerene molecules can be encapsulated per micellar aggregate.[7] The resulting fullerene/block copolymer assemblies represent new supramolecular materials with potential electronic, optoelectronic, and nonlinear optical properties.

Conclusions

Our studies of new rod-coil block copolymers have discovered novel supramolecular self-assembly features and self-organized mesostructures with size scale in the 100 nm to 200 μm range. The self-organized discrete objects are the largest outside of living systems. In the case of rod-coil diblock copolymers, they have been observed to undergo hierarchical self-assembly in a selective solvent for the coil block to periodic mesoporous materials.[2] In a selective solvent for the rodlike block the same diblocks have solubilized and encapsulated millions and billions of fullerene molecules.[1,7]

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References

(1) Jenekhe, S. A.; Chen, X. L. *Science* **1998**, *279*, 1903.

(2) Jenekhe, S. A.; Chen, X. L. *Science* **1999**, *283*, 372.

(3) Muthukumar, M.; Ober, C. K.; Thomas, E. L. *Science* **1997**, *277*, 1225.

(4) (a) Halperin, A. *Macromolecules* **1990**, *23*, 2724; (b) Semenov, A. N. *Mol. Cryst. Liq. Cryst.* **1991**, *209*, 191; (c) Raphael, E.; de Gennes, P. G. *Makromol. Chem. Macromol. Symp.* **1992**, *62*, 1; (d) Williams, D. R. M.; Fredrickson, G. H. *Macromolecules* **1992**, *35*, 3561.

(5) (a) Chen, J. T.; Thomas, E. L.; Ober, C. K.; Mao, G.-P. *Science* **1996**, *273*, 343; (b) Douy, A.; Gallot, B. *Polymer* **1987**, *28*, 147.

(6) Chen, X. L.; Jenekhe, S. A. *J. Am. Chem. Soc.*, to be submitted.

(7) Chen, X. L.; Jenekhe, S. A. *Langmuir*, submitted.

(8) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 895.

(9) (a) Jenekhe, S. A.; Zhang, X.; Chen, X. L.; Choong, V.-E.; Gao, Y.; Hsieh, B. R. *Chem. Mater.* **1997**, *9*, 409; (b) Zhang, X.; Shetty, A. S.; Jenekhe, S. A. *Acta Polymerica* **1998**, *49*, 52.

(10) Agrawal, A. K.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *J. Phys. Chem.* **1992**, *96*, 2837.

(11) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1996**, *8*, 579.

(12) Abkowitz, M. A.; Stolka, M.; Antoniadis, H.; Agrawal, A. K.; Jenekhe, S. A. *Solid State Commun.* **1992**, *83*, 937.

(13) Jenekhe, S. A.; Wynne, K. J., Eds. *Photonic and Optoelectronic Polymers*, American Chemical Society: Washington, DC, 1997.

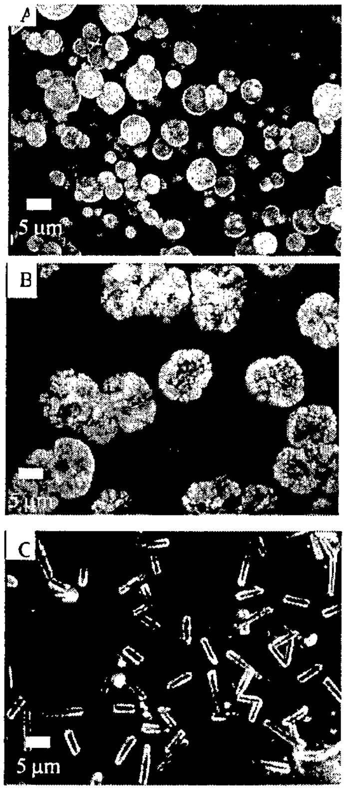

Figure 1. Fluorescence photomicrographs of micellar aggregates of diblock **1a** from TFA/dichloromethane solutions.

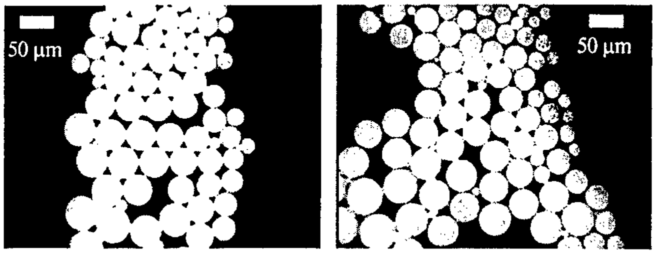

Figure 2. Fluorescence photomicrographs of vesicles self-assembled from triblock **2a** in TFA/dichloromethane solutions.