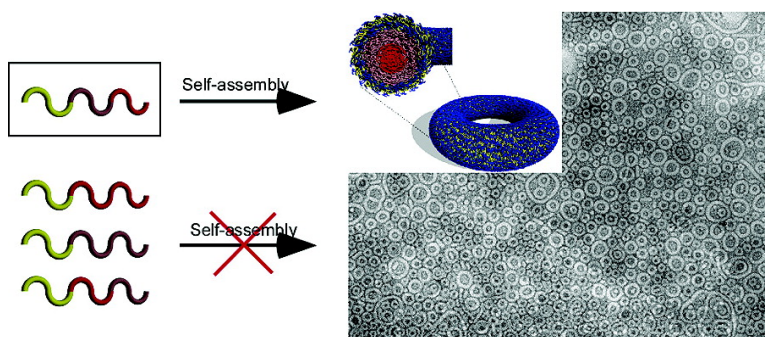


## Unique Toroidal Morphology from Composition and Sequence Control of Triblock Copolymers

Zhiyun Chen, Honggang Cui, Kelly Hales, Zhibin Li, Kai Qi, Darrin J. Pochan, and Karen L. Wooley

*J. Am. Chem. Soc.*, **2005**, 127 (24), 8592-8593 • DOI: 10.1021/ja050290p • Publication Date (Web): 25 May 2005

Downloaded from <http://pubs.acs.org> on March 25, 2009



### More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 28 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

## Unique Toroidal Morphology from Composition and Sequence Control of Triblock Copolymers

Zhiyun Chen,<sup>†</sup> Honggang Cui,<sup>‡</sup> Kelly Hales,<sup>‡</sup> Zhibin Li,<sup>‡</sup> Kai Qi,<sup>†</sup> Darrin J. Pochan,<sup>\*,‡</sup> and Karen L. Wooley<sup>\*,†</sup>

Center for Materials Innovation and Department of Chemistry, Washington University in Saint Louis, Saint Louis, Missouri 63130, and Materials Science and Engineering and Delaware Biotechnology Institute, University of Delaware, Newark, Delaware 19716

Received January 16, 2005; E-mail: klwooley@artsci.wustl.edu

Fundamental studies of the solution-state self-assembly of synthetic block copolymers have provided structural controls for the preparation of well-defined nanoscopic objects.<sup>1–7</sup> With increased understanding of the principles that govern supramolecular assemblies, in both synthetic and natural materials,<sup>8–13</sup> have also come numerous efforts and great prospects toward the development of such nanostructures as drug delivery vessels,<sup>14–16</sup> magnetic materials,<sup>17</sup> templates for biomineralization,<sup>18,19</sup> and other functional materials.<sup>20</sup>

Various morphologies, mainly spherical micelles,<sup>2,21</sup> wormlike micelles,<sup>22,23</sup> and vesicles,<sup>24,25</sup> have been observed for amphiphilic diblock copolymers undergoing supramolecular assembly in selective solvents, whereas the phase behaviors of triblock copolymers in solution have been explored<sup>26–29</sup> to a lesser extent. Triblock copolymers possess additional complexity, relative to diblock copolymers, resulting from three polymer–polymer Flory–Huggins interaction parameters  $\chi$  (instead of one in diblock copolymers), and other effects from the conditions utilized for solution-state assembly and the block copolymer architecture. Our interest has been directed toward the development of methodologies to exercise control over these complicated, yet intriguing, variables to fine-tune and access specific and novel morphologies.<sup>30,31</sup>

A unique toroidal (ring-like) morphology was reported recently, as originating from triblock copolymers comprised of acrylic acid, methyl acrylate, and styrene chain segments.<sup>31</sup> The ability to form toroids was dependent upon various parameters, including the presence of divalent counterions and the use of a mixture of solvent and nonsolvent. However, the kinetics and thermodynamics for toroid assembly, the compositional and structural requirements for assembling block copolymers, and the morphological stabilities require further investigation.<sup>32</sup>

In this study, the effects of block copolymer composition and sequence upon the resulting solution-state supramolecular assemblies were evaluated by examining four block copolymers under continuously evolving solvent conditions. These four amphiphilic block copolymers, prepared by atom transfer radical polymerization, share identical hydrophilic poly(acrylic acid) (PAA) segments and have hydrophobic segment(s) of comparable lengths, but differing in either hydrophobic segment composition or sequence (Figure 1). The design of these block copolymers is based upon the original finding of toroidal assemblies for triblock copolymer **1**, when in the presence of 2,2'-(ethylenedioxy)diethylamine (EDDA) in mixtures of tetrahydrofuran and water. The two diblock copolymer analogues, **2** and **3**, have only one of the two hydrophobic segments, either polystyrene (PS) or poly(methyl acrylate) (PMA), of overall hydrophobic block length being comparable to that of the triblock.

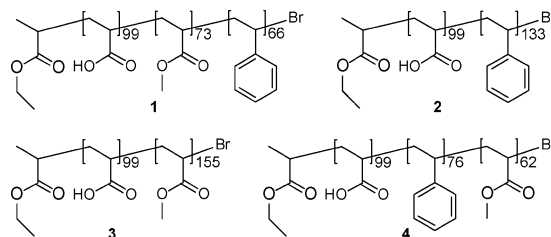


Figure 1. Structures of the block copolymers.

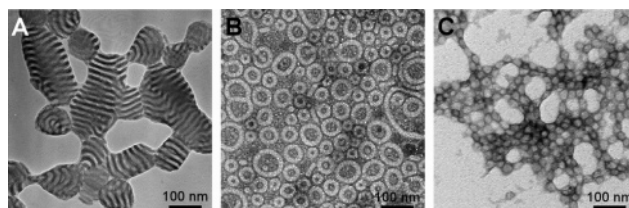


Figure 2. TEM images of **1**. THF content is 67% (A), 33% (B), and 20% (C) in H<sub>2</sub>O.

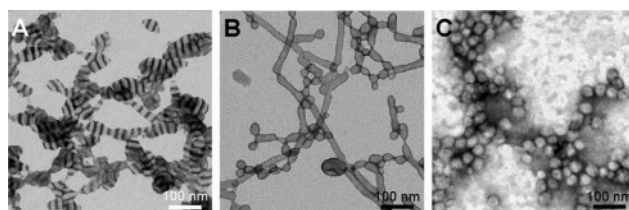


Figure 3. TEM images of **2** (A and B) and **3** (C). THF content is 67% (A), 33% (B), and 50% (C) in H<sub>2</sub>O.

Triblock copolymer **4** is essentially a constitutional isomer of **1** with reversed topological sequence of the two hydrophobic segments. All assemblies were performed under the same protocol.<sup>33</sup>

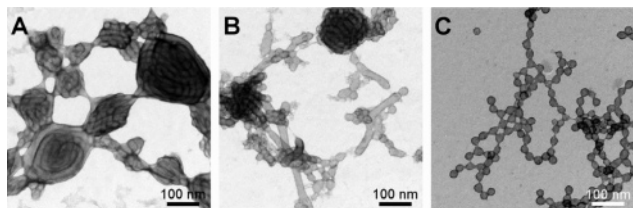
Transmission electron microscopy (TEM) images<sup>34</sup> of **1** ( $M_n = 20\,400$  Da,  $M_w/M_n = 1.05$ ), following self-assembly in tetrahydrofuran/water (THF/H<sub>2</sub>O) mixtures in the presence of EDDA, show transition of the morphologies from lamellar-type aggregates (Figure 2A) to toroids (Figure 2B) to spheres (Figure 2C) with decreasing THF content in the solution mixtures with H<sub>2</sub>O.

The self-assembly of **2** ( $M_n = 21\,200$  Da,  $M_w/M_n = 1.07$ ) produced lamellar-type aggregates at high THF content (Figure 3A), similar to those observed for **1**, but with limited dimensions. The coexistence of cylindrical and spherical micelles was observed and persisted at lower THF content (Figure 3B). At no solvent composition was the toroidal morphology observed. Only spheres were observed in the self-assembly of **3** ( $M_n = 20\,700$  Da,  $M_w/M_n = 1.09$ ) at all solution conditions (Figure 3C).

Heterogeneous aggregates were obtained from **4** ( $M_n = 20\,600$  Da,  $M_w/M_n = 1.06$ ) at high THF content (Figure 4A). With

<sup>†</sup> Washington University.

<sup>‡</sup> University of Delaware.



**Figure 4.** TEM images of **4**. THF content is 67% (A), 50% (B), and 33% (C) in H<sub>2</sub>O.

decreasing THF content relative to water, cylindrical and spherical micelles coexisted (Figure 4B), and only spheres were observed below 50 vol % THF/H<sub>2</sub>O (Figure 4C).

Interfacial energy between unlike blocks, chain stretching, solvent selectivity, and coronal interaction can be considered, qualitatively, to explain differences in the observed morphologies. Because the four block copolymers share identical hydrophilic segments, the interactions between the corona are comparable. Therefore, the morphological differences observed for their assemblies in THF/H<sub>2</sub>O solutions should be dependent upon the nature of the core material and the interfacial energy differences between the corona and core materials. The assembly behavior for **3** differed significantly, in comparison to that of the other three block copolymers (Figure 3C), which can be explained by the interfacial energy and solubility differences between PAA, PMA, and PS. The interfacial energy is less between PAA and PMA than between PAA and PS, thus less interfacial curvature is provided for PAA/PS than for PAA/PMA and cylinders are preferred for **2** versus **3**. Additionally, THF is slightly selective for PS, which allows for greater hydrophobic core volume in assemblies of **2** versus **3**. This difference in core swelling produces a lower interfacial curvature in **2** versus **3** and the consequent formation of cylinders versus exclusively spheres, respectively. Interestingly, **4** did not exhibit a toroidal morphology, which indicates the importance of the block copolymer sequence. Apparently, collapse of the intermediary PS segment of **4** limits the accessible morphologies, whereas PMA can serve as a flexible boundary layer between PAA and PS to facilitate curvature of the cylindrical structure into toroids, as observed for **1**. The different self-assembly behaviors between triblock copolymer **1** and diblock copolymer **2** can also be explained by this flexible boundary layer, in addition to complex interfacial energy differences.

In conclusion, studies to probe the assembly of diblock and triblock copolymers under the same solution-state conditions have revealed that the unique toroidal morphology is dependent upon block copolymer composition and sequence. Toroid formation was successful only for an amphiphilic triblock copolymer having a terminal hydrophilic PAA segment undergoing self-attraction by EDDA serving as a divalent counterion, an intermediate flexible PMA sequence serving as a flexible domain, and a terminal rigid, hydrophobic PS segment that can collapse to constitute a core. We continue to investigate the kinetics of these assembly processes and their reversibilities. Although toroidal assemblies are common for DNA and other biological macromolecules, the ability to tune the morphology of synthetic materials offers significant latitude in the types of materials, their properties, and their utility.

**Acknowledgment.** This material is based upon work supported by the National Science Foundation under Grant Nos. 0210247 and 0301833. We also thank the W. M. Keck College of Engineering electron microscopy lab at the University of Delaware, nuclear magnetic resonance facilities of the Department of Chemistry, and TEM facilities of Department of Physics at Washington University in Saint Louis.

**Supporting Information Available:** Experimental details for the preparation, characterization, and assembly of the block copolymers **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31.
- (2) Prochazka, K.; Martin, T. J.; Munk, P.; Webber, S. E. *Macromolecules* **1996**, *29*, 6518.
- (3) Stupp, S. I.; LeBonheur, V.; Walker, K.; Li, L. S.; Huggins, K. E.; Keser, M.; Amstutz, A. *Science* **1997**, *276*, 384.
- (4) Shen, H.; Eisenberg, A. *Macromolecules* **2000**, *33*, 2561.
- (5) Discher, D. E.; Eisenberg, A. *Science* **2002**, *297*, 967.
- (6) Yan, X.; Liu, G.; Li, Z. *J. Am. Chem. Soc.* **2004**, *126*, 10059.
- (7) Jain, S.; Bates, F. S. *Science* **2003**, *300*, 460.
- (8) Cornelissen, J. J. L. M.; Fischer, M.; Sommerdijk, N. A. J. M.; Nolte, R. J. M. *Science* **1998**, *280*, 1427.
- (9) Lodge, T. P.; Hillmyer, M. A.; Zhou, Z.; Talmon, Y. *Macromolecules* **2004**, *37*, 6680.
- (10) Bates, F. S. *Science* **1991**, *251*, 898.
- (11) Bellomo, E. G.; Wyrsta, M. D.; Pakstis, L.; Pochan, D. J.; Deming, T. J. *Nat. Mater.* **2004**, *3*, 244.
- (12) Thordarson, P.; Coumans, R. G. E.; Elemans, J. A. A. W.; Thomassen, P. J.; Visser, J.; Rowan, A. E.; Nolte, R. J. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 4755.
- (13) Vriezema, D. M.; Kros, A.; de Gelder, R.; Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M. *Macromolecules* **2004**, *37*, 4736.
- (14) Ahmed, F.; Discher, D. E. *J. Controlled Release* **2004**, *96*, 37.
- (15) Pan, D.; Turner, J. L.; Wooley, K. L. *Chem. Commun.* **2003**, *19*, 2400.
- (16) Rosler, A. V.; Guido W. M.; Klok, H.-A. *Adv. Drug Delivery Rev.* **2001**, *53*, 95.
- (17) Clendenning, S. B.; Fourmier-Bidoz, S.; Pietrangelo, A.; Yang, G.; Han, S.; Brodersen, P. M.; Yip, C. M.; Lu, Z.-H.; Ozin, G. A.; Manners, I. J. *Mater. Chem.* **2004**, *14*, 1686.
- (18) Hartgerink, J. D.; Beniash, E.; Stupp, S. I. *Science* **2001**, *294*, 1684.
- (19) Li, M.; Cölfen, H.; Mann, S. *J. Mater. Chem.* **2004**, *14*, 2269.
- (20) Li, L.; Beniash, E.; Zubarev, E. R.; Xiang, W.; Rabatic, B. M.; Zhang, G.; Stupp, S. I. *Nat. Mater.* **2003**, *2*, 689.
- (21) Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728.
- (22) Bronich, T. K.; Popov, A. M.; Eisenberg, A.; Kabanov, V. A.; Kabanov, A. V. *Langmuir* **2000**, *16*, 481.
- (23) Dalhaimer, P.; Bermudez, H.; Discher, D. E. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 168.
- (24) Terreau, O.; Luo, L.; Eisenberg, A. *Langmuir* **2003**, *19*, 5601.
- (25) Discher, B. M.; Won, Y.-Y.; Ege, D. S.; Lee, J. C.-M.; Bates, F. S.; Discher, D. E.; Hammer, D. A. *Science* **1999**, *284*, 1143.
- (26) Yu, G.-e.; Eisenberg, A. *Macromolecules* **1998**, *31*, 5546.
- (27) Zhou, Z.; Li, Z.; Ren, Y.; Hillmyer, M. A.; Lodge, T. P. *J. Am. Chem. Soc.* **2003**, *125*, 10182.
- (28) Liu, S.; Armes, S. P. *J. Am. Chem. Soc.* **2001**, *123*, 9910.
- (29) Ma, Q.; Remsen, E. E.; Clark, C. G., Jr.; Kowalewski, T.; Wooley, K. L. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5058.
- (30) Li, Z.; Kesselman, E.; Talmon, Y.; Hillmyer, M. A.; Lodge, T. P. *Science* **2004**, *306*, 98.
- (31) Pochan, D. J.; Chen, Z.; Cui, H.; Hales, K.; Qi, K.; Wooley, K. L. *Science* **2004**, *306*, 94.
- (32) Jain, S.; Bates, F. S. *Macromolecules* **2004**, *37*, 1511.
- (33) The block copolymer (ca. 0.1 wt %) and EDDA (1:1, amine:acrylic acid) were allowed to dissolve in THF. H<sub>2</sub>O was then added slowly (ca. 75% of initial volume per hour) until the desired solution composition was obtained.
- (34) All samples were deposited from the solvent mixtures onto carbon-coated copper grids and were negatively stained by uranyl acetate.

JA050290P