DOI: 10.1002/anie.200806051

Bamboo-like Structures

Undulated Multicompartment Cylinders by the Controlled and Directed Stacking of Polymer Micelles with a Compartmentalized Corona**

*Bing Fang, Andreas Walther, Andrea Wolf, Youyong Xu, Jiayin Yuan, and Axel H. E. Müller**

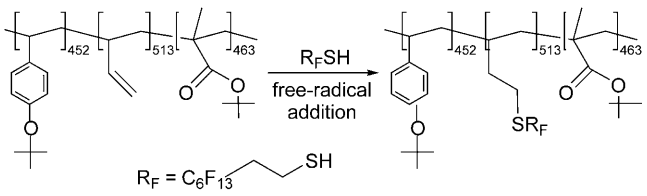
Self-assembled nanostructures from diblock copolymers have been intensively investigated during the last decade,[1–4] with studies being driven by scientific interest and potential applications. Self-assembled structures that are constructed from ABC block terpolymers are even more promising, because of the additional parameters introduced by the third block.[5–13] Depending on the solubility character of the three blocks, micelles formed by block terpolymers can be divided into two classes: micelles with a compartmentalized core[11,14–16] and with a compartmentalized corona.[17–28] In the second class, micellar structures with noncentrosymmetric coronas—Janus particles[29]—are particularly interesting because of their appealing properties, and have been targeted by us[20,23,30] and other research groups.[24,31] Most of the strategies for the preparation of these Janus particles transfer the morphologies of well-defined bulk structures into solution by controlled cross-linking processes.[32–34]

The requirement of the corona-forming blocks to undergo phase-segregation is the most challenging aspect of the creation of micelles with compartmentalized coronas based on the pure self-assembly of either block terpolymers, or a combination of two diblock copolymers in solution.[35] The phase separation of two blocks in solution is, however, not as pronounced as in the bulk state. Copolymers with fluorinated and nonfluorinated blocks are known to undergo phase segregation in the bulk state[36] and in solution[37] because of the unique solubility characteristics of fluorinated structures, such as high hydrophobicity and lipophobicity. Therefore, it is reasonable to expect that a fluorinated block can serve as the core of a micelle in organic media without requiring chemical cross-links.

Herein, we report the formation of micelles with compartmentalized coronas by the self-assembly of a specifically designed block terpolymer, poly(4-*tert*-butoxystyrene)-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) (PtBS–PB–PtBMA), where the central PB block was modified with a fluorinated side group by the thiol–ene reaction of the vinyl groups with 1-mercapto-1*H*,1*H*,2*H*,2*H*-perfluorooctane (see the Supporting Information). In organic, fluorophobic media, the fluorinated block acts as a micellar core and allows sufficient dynamics for reorientation during annealing. In dioxane, a common solvent for both outer blocks, micelles with patchy coronas are obtained. Subsequent transfer into a selective solvent for the PtBMA block induces aggregation into branched, undulated cylinders with a multicompartment character. The overall process to achieve the required structures involves only moderately complex polymer architectures and a simple preparation method in solution. To date, structures with similarly complex features were obtained only by using more complex procedures or polymer architectures. For instance, Li et al. prepared wormlike structures with segmented cores from discrete multicompartment micelles of miktoarm star terpolymers.[38] Similar structures reported by Cui et al. require organic diamines and a special swelling solvent to achieve a kinetically controlled assembly of micelles with PAA coronas.[39] Our strategy for stacking micelles with compartmentalized coronas does not require complicated polymer structures, small molecules, or swelling solvents.

The fluorination (Scheme 1) of the PtBS–PB–PtBMA block terpolymer alters the solubility of the middle block in dioxane, a fluorophobic solvent. The unmodified block terpolymers, which are initially molecularly dispersed, form micelles with fluorinated segments as cores. Micelle formation was shown to occur by using transmission electron microscopy (TEM) and dynamic light scattering (DLS). TEM images of the micelles in dioxane, after annealing at 75 °C for 48 h, are shown in Figure 1.

The micelles obtained have a narrow size distribution (see Figure 1 a, $R_{h,DLS} \approx 62$ nm, PDI = 1.03) and are of an overall spherical shape. The sizes measured by using TEM appear



Scheme 1. Molecular structures of original and the fluoroalkyl-modified PtBS–PB–PtBMA block terpolymer.

[*] B. Fang, Dr. A. Walther, Dipl.-Chem. A. Wolf, Dr. Y. Xu, J. Yuan, Prof. Dr. A. H. E. Müller
Makromolekulare Chemie II and Bayreuther Zentrum für Kolloide und Grenzflächen, Universität Bayreuth
95440 Bayreuth (Germany)
Fax: (+49) 921-55-3393
E-mail: axel.mueller@uni-bayreuth.de

[**] B.F. acknowledges a DAAD Scholarship within the Sandwich Program. A.W. thanks the Bavarian Elite Support Program for a scholarship.

Supporting information for this article (experimental section, AFM and SEM images of the undulated cylinders, and TEM images of the micelles before the annealing procedure and their large spherical aggregates in ethanol) is available on the WWW under http://dx.doi.org/10.1002/anie.200806051.

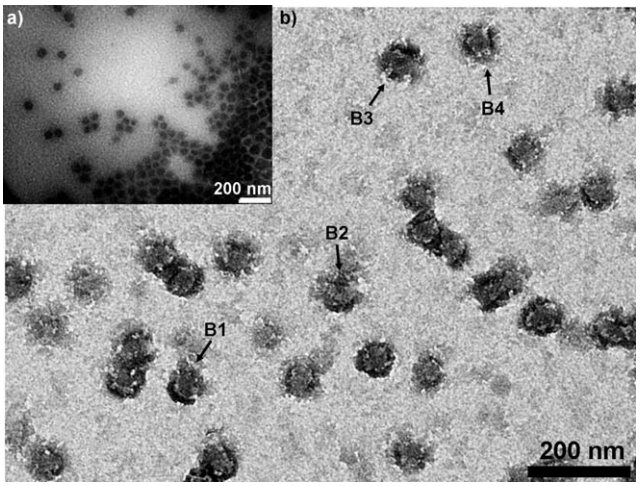


Figure 1. a) Nonstained and b) RuO_4 stained TEM images of individual micelles obtained by drop coating from dioxane onto a carbon-coated TEM grid after annealing.

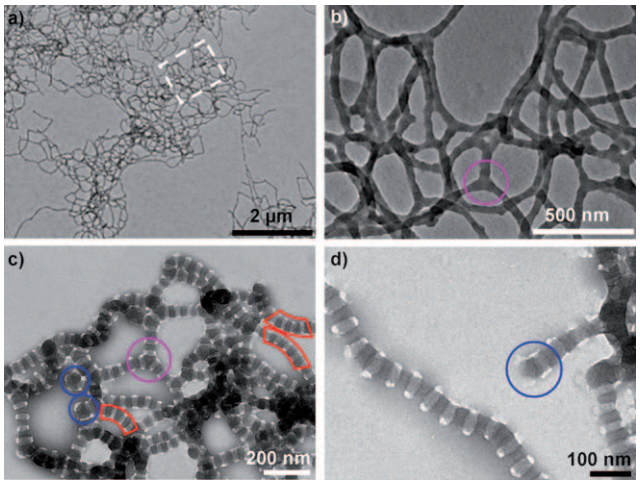


Figure 2. a, b) Nonstained and c, d) RuO_4 stained TEM images of undulated cylinders, obtained from ethanol.

smaller than the average sizes calculated from DLS because of the collapse of the well-solubilized corona during solvent removal during the TEM sample preparation. Although fluorinated structures can potentially access the super-strong segregation limit[11] and give rise to stable disclike structures, large disclike particles were not observed.

To gain further insights into the micelle structure, selective staining of the PtBS section was performed using RuO_4. Figure 1b shows that the micelles are only partially stained, which clearly indicates that the corona has a patchy structure that arises from phase segregation. The number of patches varies and the system does not adopt a completely uniform structure, even after annealing for 48 h. The distribution of patch sizes is due to an interplay of interfacial energy minimization and entropy maximization. We mainly found two varieties of micelles with one or two patches. The first variety represents a Janus micelle (B1, Figure 1b), the second variety consists of micelles with different spatial patch distributions (B2, B3, B4, Figure 1b).

Dialysis was subsequently used to exchange dioxane with ethanol, which is a nonsolvent for PtBS but dissolves PtBMA. The annealing step proved to be crucial for a reorganization of the corona to direct a further self-assembly process of the block terpolymer micelles on a second length scale. For instance, when the solution of the micelles in dioxane was directly dialyzed against ethanol without annealing, only large, ill-defined spherical aggregates were formed (see Figure S3 in the Supporting Information). However, when an annealing procedure was performed, TEM images show that the micelles are organized into cylindrical aggregates (Figure 2), which extend over several micrometers and exhibit branching points and end caps. Even without staining, the images show some weak, well-spaced undulations along their major axis, which originate from a regular packing within the cylinders, and are similar to the surfaces of bamboo rods. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies also show similar images (see Figure S1 and S2 in the Supporting Information).

Phase separation into patches, which is induced by annealing, guides the further stacking of the micelles when the solvent is changed to a selective one. The slightly darker microdomains visible in the nonstained image of the cylinders in Figure 2b represent the location of the micellar cores. The contrast in the TEM images is highest for the fluorinated segment. This internal structure can be amplified and switched in terms of brightness by staining with RuO_4 (Figure 2c,d). The corresponding TEM images show cylindrical assemblies with alternating dark and light segments, which arise from the strong staining of the PtBS domains. The red, pink, and blue colored regions indicate cylinders, branching points, and end caps, respectively. Before staining, the junction is composed of a light section surrounded by three dark sections (Figure 2b), however, after staining, the contrast is completely reversed (Figure 2c). Since staining darkens the PtBS patches, the fluorinated segments appear relatively lighter. Thus, the PtBS patches act as the connecting parts of the micelles and also form the junctions. Furthermore, it is obvious that the ends of the undulated cylinders are formed by connection of several micelles. A thorough phase separation of the corona (Janus-type) leads to the formation of end caps on the extending cylinders and prevents further stacking.

Interestingly, the aggregation process is reversible. The micelles ($R_h \approx 62$ nm, PDI = 1.03, DLS) can be recovered when the solvent is changed from ethanol back to dioxane. In order to explain the observed aggregation behavior, we suggest the following mechanism (Figure 3). The initially formed micelles with mixed coronas of PtBS and PtBMA undergo microdomain phase separation within the corona to achieve energetically more favorable states upon annealing.

As well as the expected micelles with Janus-type coronas (species A, Figure 3), which undergo complete phase separation, micelles with incompletely phase-separated coronas also exist (species B, C, and D). As a consequence of the phase-segregation within the corona, the micelles aggregate into a stacked, multicompartment morphology (undulated cylinders) in ethanol as a selective solvent. Since linear assembly

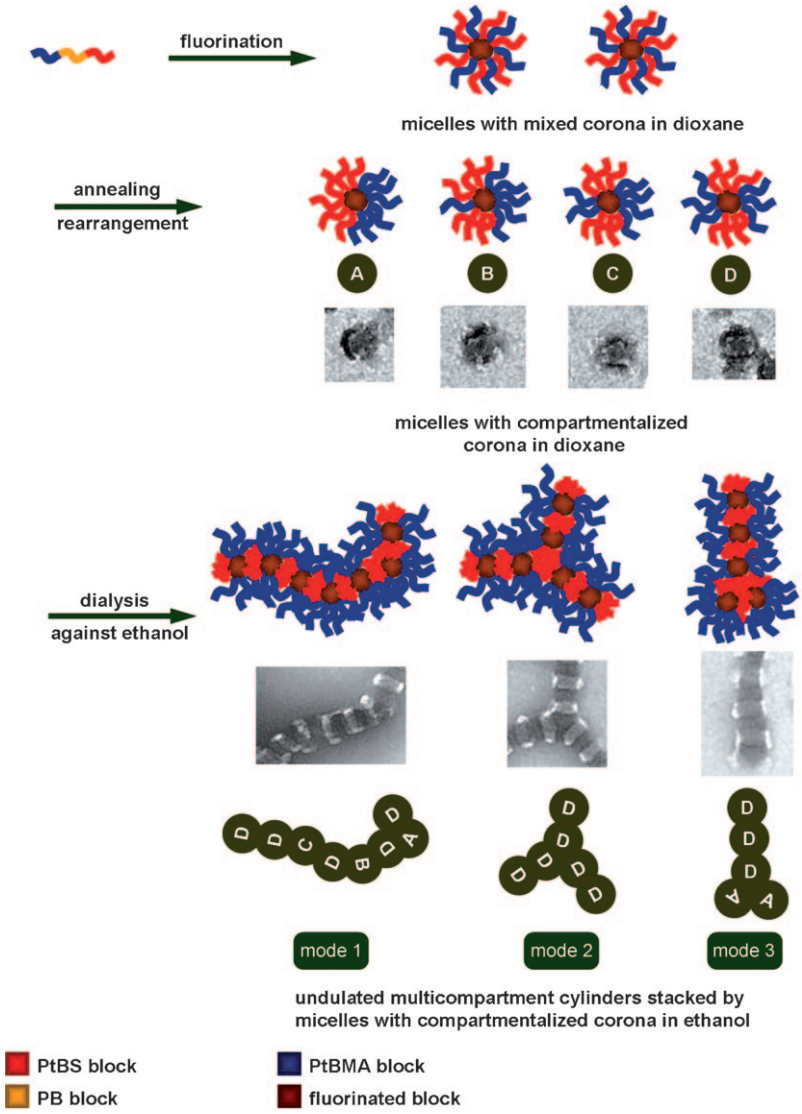


Figure 3. Preparation of undulated multicompartment cylinders by directed stacking polymer micelles with compartmentalized corona.

prevails and because of the fact that the branch points are composed of PtBS (and not fluorinated PB) segments, the micelles mainly exhibit two patches of the PtBS. The extent of phase segregation and the distribution of the patches define the different connecting modes, as shown in Figure 3 (modes 1, 2, and 3). The modes represent extended undulated cylinders (red regions in Figure 2c), branching points (pink regions in Figure 2b,c) and end caps (blue regions in Figure 2c,d).

In conclusion, PtBS–PB–PtBMA block terpolymers were modified with a fluoroalkyl group on the PB block. In dioxane solution, these terpolymers formed micelles with a fluorinated PB core and a compartmentalized corona, obtained by microdomain phase separation of the PtBS and PtBMA blocks upon annealing. Bamboo-like, undulated cylindrical assemblies were obtained by stacking of the micelles in ethanol, which is a selective solvent for PtBMA. The cylinders have uniform diameters and are connected with each other by junctions to form branched giant assemblies. Imaging data confirm the formation of the undulated cylinders. Selective staining of the PtBS sections enabled a clear deduction of the internal structure and the patchy character of the corona. The cylinders can be reverted to micelles by dialysis against dioxane, which indicates that the stacking of the micelles is a reversible process. The association of compartmentalized micelles into branched structures can also provide an insight into the use of 3D sol–gel methods in materials synthesis, and furthermore a facile approach to the preparation of multicompartment superstructures has been made available. Variation of the monomers and the weight fractions of the constituents should enable the tuning of the aggregate structures. Further investigations are focused on the complete or selective hydrolysis of PtBMA and PtBS blocks for the preparation of water-soluble and pH-responsive structures, as well as their application in templating inorganic–organic hybrid materials.

Received: December 12, 2008
Revised: February 16, 2009
Published online: March 12, 2009

Keywords: aggregation · block terpolymers · micelles · self-assembly · solvent effects

[1] L. F. Zhang, A. Eisenberg, *Science* **1995**, *268*, 1728.
[2] L. Zhang, A. Eisenberg, *Polym. Adv. Technol.* **1998**, *9*, 677.
[3] G. Riess, *Prog. Polym. Sci.* **2003**, *28*, 1107.
[4] H. Mori, A. H. E. Müller, *Prog. Polym. Sci.* **2003**, *28*, 1403.
[5] S. Kubowicz, J.-F. Baussard, J.-F. Lutz, A. F. Thünemann, H. von Berlepsch, A. Laschewsky, *Angew. Chem.* **2005**, *117*, 5397; *Angew. Chem. Int. Ed.* **2005**, *44*, 5262.
[6] J. Zhu, W. Jiang, *Macromolecules* **2005**, *38*, 9315.
[7] F. Liu, A. Eisenberg, *J. Am. Chem. Soc.* **2003**, *125*, 15059.
[8] S. Stewart, G. Liu, *Angew. Chem.* **2000**, *112*, 348; *Angew. Chem. Int. Ed.* **2000**, *39*, 340.
[9] E. Discher Dennis, D. Kamien Randall, *Nature* **2004**, *430*, 519.
[10] Y. Cai, S. P. Armes, *Macromolecules* **2004**, *37*, 7116.
[11] Z. Zhou, Z. Li, Y. Ren, M. A. Hillmyer, T. P. Lodge, *J. Am. Chem. Soc.* **2003**, *125*, 10182.
[12] T. P. Lodge, M. A. Hillmyer, Z. Zhou, Y. Talmon, *Macromolecules* **2004**, *37*, 6680.
[13] J.-F. Gohy, N. Willet, S. Varshney, J.-X. Zhang, R. Jerome, *Angew. Chem.* **2001**, *113*, 3314; *Angew. Chem. Int. Ed.* **2001**, *40*, 3214.
[14] G. E. Yu, A. Eisenberg, *Macromolecules* **1998**, *31*, 5546.
[15] F. Liu, G. Liu, *Macromolecules* **2001**, *34*, 1302.
[16] X. S. Wang, M. A. Winnik, I. Manners, *Macromolecules* **2002**, *35*, 9146.
[17] A. I. Triftaridou, M. Vamvakaki, C. S. Patrickios, *Polymer* **2002**, *43*, 2921.

[18] M. Gadzinowski, S. Sosnowski, *J. Polym. Sci. Part A* **2003**, *41*, 3750.
[19] J.-F. Gohy, E. Khousakoun, N. Willet, S. K. Varshney, R. Jerome, *Macromol. Rapid Commun.* **2004**, *25*, 1536.
[20] R. Erhardt, A. Böker, H. Zettl, H. Kaya, W. Pyckhout-Hintzen, G. Krausch, V. Abetz, A. H. E. Müller, *Macromolecules* **2001**, *34*, 1069.
[21] H. Xu, R. Erhardt, V. Abetz, A. H. E. Müller, W. A. Goedel, *Langmuir* **2001**, *17*, 6787.
[22] R. Erhardt, M. Zhang, A. Böker, H. Zettl, C. Abetz, P. Frederik, G. Krausch, V. Abetz, A. H. E. Müller, *J. Am. Chem. Soc.* **2003**, *125*, 3260.
[23] Y. Liu, V. Abetz, A. H. E. Müller, *Macromolecules* **2003**, *36*, 7894.
[24] R. Saito, A. Fujita, A. Ichimura, K. Ishizu, *J. Polym. Sci. Part A* **2000**, *38*, 2091.
[25] S. I. Stupp, V. LeBonheur, K. Walker, L. S. Li, K. E. Huggins, M. Keser, A. Amstutz, *Science* **1997**, *276*, 384.
[26] G. N. Tew, L. Li, S. I. Stupp, *J. Am. Chem. Soc.* **1998**, *120*, 5601.
[27] M. U. Pralle, K. Urayama, G. N. Tew, D. Neher, G. Wegner, S. I. Stupp, *Angew. Chem.* **2000**, *112*, 1546; *Angew. Chem. Int. Ed.* **2000**, *39*, 1486.
[28] E. Hoppenbrouwers, Z. Li, G. Liu, *Macromolecules* **2003**, *36*, 876.
[29] A. Walther, A. H. E. Müller, *Soft Matter* **2008**, *4*, 663.
[30] A. Walther, X. Andre, M. Drechsler, V. Abetz, A. H. E. Müller, *J. Am. Chem. Soc.* **2007**, *129*, 6187.
[31] S. Förster, M. Antonietti, *Adv. Mater.* **1998**, *10*, 195.
[32] R. Stadler, C. Auschra, J. Beckmann, U. Krappe, I. Voigt-Martin, L. Leibler, *Macromolecules* **1995**, *28*, 3080.
[33] V. Abetz, T. Goldacker, *Macromol. Rapid Commun.* **2000**, *21*, 16.
[34] A. Walther, A. Göldel, A. H. E. Müller, *Polymer* **2008**, *49*, 3217.
[35] a) I. K. Voets, A. de Keizer, P. de Waard, P. M. Frederik, P. H. H. Bomans, H. Schmalz, A. Walther, S. M. King, F. A. M. Leermakers, M. A. Cohen Stuart, *Angew. Chem.* **2006**, *118*, 6825; *Angew. Chem. Int. Ed.* **2006**, *45*, 6673; b) A. Walther, P.-E. Millard, A. Goldmann, F. Schacher, T. M. Lovestead, C. Barner-Kowollik, A. H. E. Müller, *Macromolecules* **2008**, *41*, 8608; c) H. Schmalz, J. Schmelz, .M. Drechsler, J. Yuan, A. Walther, K. Schweimer, A. Mihut, *Macromolecules* **2008**, *41*, 3235.
[36] D. R. Iyengar, S. M. Perutz, C.-A. Dai, C. K. Ober, E. J. Kramer, *Macromolecules* **1996**, *29*, 1229.
[37] K. Matsumoto, H. Mazaki, H. Matsuoka, *Macromolecules* **2004**, *37*, 2256.
[38] Z. Li, E. Kesselman, Y. Talmon, M. A. Hillmyer, T. P. Lodge, *Science* **2004**, *306*, 98.
[39] H. Cui, Z. Chen, S. Zhong, K. L. Wooley, D. J. Pochan, *Science* **2007**, *317*, 647.

