Communication

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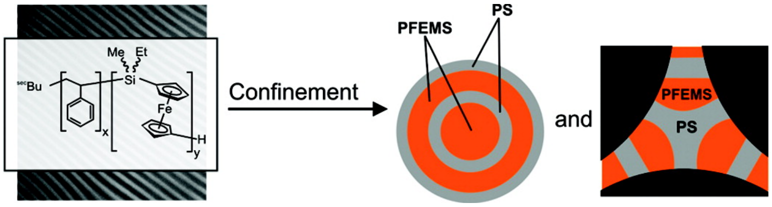

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Block Copolymers under Periodic, Strong Three-Dimensional Confinement

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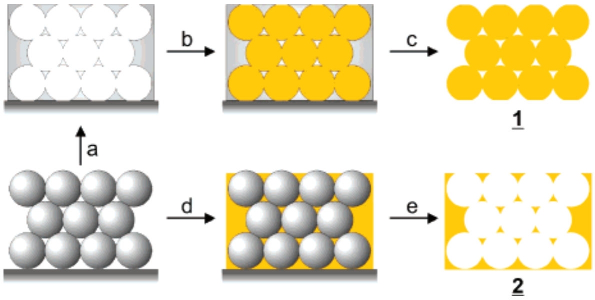
Diblock copolymers, composed of two covalently linked, incompatible polymer segments, are well-known to undergo microphase separation in both bulk and thin films to give periodic morphologies such as ordered spheres, cylinders, and lamellae.[1] However, it is only recently that the influences of confinement and boundary conditions on block copolymer self-assembly have been investigated. When these materials are cast onto supports having certain directing features, either topological or chemical, the self-assembly process can be strongly influenced when the features approach the length of the equilibrium periodicity of the block copolymer domains. For instance, a block copolymer film can experience confinement due to a finite thickness[2] or due to the presence of a chemical pattern on a planar substrate.[3] When cast on a substrate with structural topography[4] or within microchannels,[5] the orientation of domains can be directed by the vertical walls. By self-assembling block copolymers within small linear channels, as in nanoporous alumina, confinement effects can be dramatic, leading to unexpected morphologies such as stacked disks or spirals.[6] Unexplored to date is the 3D confinement of block copolymers, which could offer exciting opportunities for both the manipulation of classical phase separated morphologies and the discovery of new periodic phases.

In this study we investigate the self-assembly of diblock copolymers within the nanoscale periodic voids of colloidal crystal (CC) templates. CCs can be obtained from the self-assembly of ceramic or polymeric microspheres,[7] and these can in turn generate inverse CCs through a templating approach.[8] In both cases, the periodic voids present a large surface-to-volume ratio and are expected to strongly influence the self-assembly of block copolymers through interfacial interactions. Further interest arises when one of the polymer blocks is a metal-rich segment as in the well-studied polyferrocenylsilane.[9] Such block copolymers are readily available from living anionic ring-opening polymerization of ring-strained sila[1]ferrocenophanes[10] and offer useful redox properties[11] and the ability to generate magnetic ceramics and catalysts upon pyrolysis.[12,13]

Our approach in this work is illustrated in Scheme 1 and uses CC lattices consisting of either air spheres in a silica matrix (**CC$_{\mathbf{air}}$**) or silica spheres in an air matrix (**CC$_{\mathbf{silica}}$**). **CC$_{\mathbf{air}}$** samples are generated by self-assembly of **PS** microspheres, filling the structure by silica CVD,[14] and etching of the polymer using air plasma, while **CC$_{\mathbf{silica}}$** samples are produced by evaporation-induced self-assembly of silica microspheres.[15] As a diblock copolymer, we selected the amorphous polystyrene-*block*-polyferrocenylethylmethylsilane diblock copolymer (**PS-*b*-PFEMS**, M_n = 132 000 g/mol, PDI = 1.05, øPFEMS = 0.52), which affords well-defined lamellae in the bulk state (Figure 1). The average PFEMS and PS lamella thickness of 46 and 42 nm, respectively, and average domain spacing of 88 nm were determined by transmission electron microscopy (TEM). By slowly evaporating a dichloromethane solution of **PS-*b*-PFEMS** (20−50 mg/mL) into a CC template, the polymer effectively fills the template voids by capillary action. Self-assembly of the confined diblock copolymer is performed using a combination of solvent vapor annealing (toluene atmosphere, 3 days)[16] and thermal annealing (170−180 °C, 3 days), successful in the ordering of block copolymer morphologies.[17] Dissolution of the silica mold with aqueous HF (CAUTION: strong acid) generates **PS-*b*-PFEMS** replicas as inverse CCs (**1**) or double-inverse CCs (**2**).

Scheme 1. Preparation of 3D Confined **PS-*b*-PFEMS**[a]



[a] (a) Generation of **CC$_{\mathbf{air}}$** by silica CVD within a latex template then etching. (b, d) Capillary infiltration of **CC$_{\mathbf{air}}$** and **CC$_{\mathbf{silica}}$** with **PS-*b*-PFEMS**. (c, e) Etching of silica template by aqueous HF.

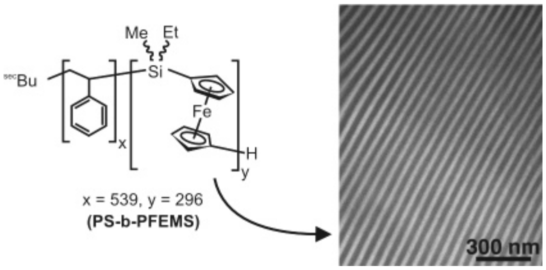


Figure 1. Bright field transmission electron micrograph of a bulk microsection of **PS-*b*-PFEMS** depicting a lamellar phase. (Light areas = **PS**, Dark areas = **PFEMS**).

Shown in Figure 2 are TEM results from sample **1**, having ordered, interconnected **PS-*b*-PFEMS** spheres ca. 210 nm in diameter surrounded by air voids. In this sample, the lamellae were clearly oriented parallel to the templating silica surfaces. While this is the conventional form of lamellar alignment, the strong curvature of the template results in the lamellae wrapping together to form concentric shells with a solid spherical center. Figure 2c shows a TEM image with superimposed EDX elemental traces, confirming the location of the **PS** and **PFEMS** blocks and the absence of the silica template. The estimated dimensions by TEM of the **PFEMS** core and subsequent shell are 98 and 38 nm, respectively, while the inner and outer **PS** shells are 25 and 14 nm, respectively. Clearly the effects of strong 3D confinement have altered both the morphology and dimensions of the lamellar diblock copolymer in comparison to its equilibrium bulk state. It is very difficult to predict whether the morphology observed in **1** is the expected structure. In addition to surface wetting of the silica

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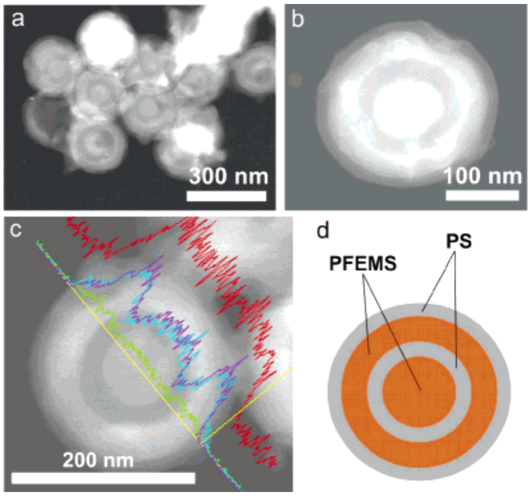

Figure 2. TEM analysis of sample **1**. (a and b) Low and high magnification dark-field TEM images, respectively, for **PS-*b*-PFEMS** colloidal crystal. (c) Dark-field TEM image of sample **1**, with TEMEDX traces for carbon (red), silicon (turquoise), iron (purple), and oxygen (green). (Dark areas = **PS**, Light areas = **PFEMS**.) (d) Schematic diagram of architecture shown in (c).

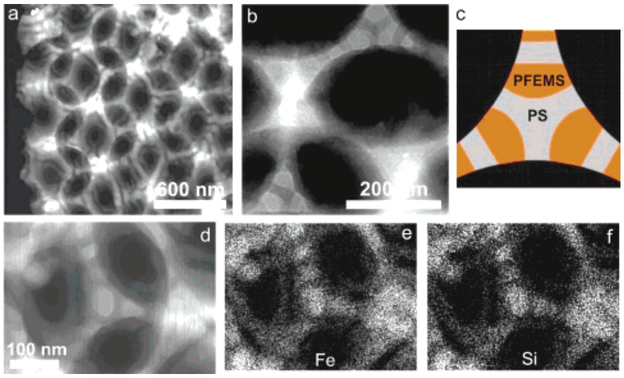

Figure 3. TEM analysis of sample **2**. (a) Low and (b and d) high magnification dark-field TEM images. (c) Schematic of block copolymer morphology in section of (b). (e and f) TEM-EDX traces for Fe and Si, respectively, in the area corresponding to (d). (Dark areas = **PS**, Light areas = **PFEMS**.)

template, self-assembly is likely influenced by the strong curvature of the void spaces as well as "communication" with 12 adjacent voids through interconnecting windows.

The confinement behavior is even more pronounced when we look at sample **2** (Figure 3), consisting of a matrix of **PS-*b*-PFEMS** surrounding ordered spherical voids ca. 375 nm in diameter. Microphase-separated morphologies are clearly visible in TEM images and are highly unusual. Because of the strong confinement imposed by the surrounding silica spheres, the lamellae orient themselves orthogonal to the sphere surfaces instead of in a parallel arrangement most common in lamellar phases.[18] The block assignment was confirmed by EDX mapping, with Fe and Si distribution maps (Figure 3, parts e and f, respectively) showing the location of the **PFEMS** segments. The periodic and interconnected nature of the template forces the lamellae to curve, branch and join, forming a phase that follows the topology of the void space, and thus these do not easily lend themselves to a width estimation. Nevertheless, TEM-estimated dimensions of the curved "lamellar-like" **PFEMS** and **PS** domains are similar to those of the respective inner shells found in **1**.

The strong topological modulation within colloidal crystals makes them perfect templates for studying the effects of 3D confinement on block copolymer self-assembly. Further studies using templates of different sizes and block copolymers with different volume fractions will likely uncover a plethora of unusual and unexpected morphologies. Such studies could be of prime importance in both the fundamental understanding of self-assembly and in generating unique ordered phases that could be useful in generating complex photonic crystals for optical applications.

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References

(1) Park, C.; Yoon, J.; Thomas, E. L. *Polymer* **2003**, *44*, 6725–6760.
(2) Fasolka, M. J.; Mayes, A. M. *Annu. Rev. Mater. Res.* **2001**, *31*, 323–355.
(3) Kim, S. O.; Solak, H. H.; Stoykovich, M. P.; Ferrier, N. J.; de Pablo, J. J.; Nealey, P. F. *Nature* **2003**, *424*, 411–414.
(4) (a) Cheng, J. Y.; Mayes, A. M.; Ross, C. A. *Nat. Mater.* **2004**, *3*, 823–828. (b) Segalman, R. A.; Yokoyama, H.; Kramer, E. J. *Adv. Mater.* **2001**, *13*, 1152–1155. (c) Cheng, J. Y.; Ross, C. A.; Thomas, E. L.; Smith, H. I.; Vancso, G. J. *Adv. Mater.* **2003**, *15*, 1599–1602.
(5) (a) Li, H.-W.; Huck, W. T. S. *Nano Lett.* **2004**, *4*, 1633–1636. (b) Cheng, J. Y.; Ross, C. A.; Thomas, E. L.; Smith, H. I.; Vancso, G. J. *Appl. Phys. Lett.* **2002**, *81*, 3657–3659.
(6) (a) Wu, Y.; Cheng, G.; Katsov, K.; Sides, S. W.; Wang, J.; Tang, J.; Fredrickson, G. H.; Moskovits, M.; Stucky, G. D. *Nat. Mater.* **2004**, *3*, 816–822. (b) Shin, K.; Xiang, H.; Moon, S. I.; Kim, T.; McCarthy, T. J.; Russell, T. P. *Science* **2004**, *306*, 76.
(7) (a) López, C. *Adv. Mater.* **2003**, *15*, 1679–1704. (b) Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. *Adv. Mater.* **2000**, *12*, 693–713.
(8) (a) Holland, B. T.; Blanford, C. F.; Stein, A. *Science* **1998**, *281*, 538–540. (b) Wijnhoven, J. E. G. J.; Vos, W. L. *Science* **1998**, *281*, 802–804. (c) Blanco, A.; Chomski, E.; Grabtchak, S.; Ibisate, M.; John, S.; Leonard, S. W.; López, C.; Meseguer, F.; Miguez, H.; Mondia, J. P.; Ozin, G. A.; Toader, O.; van Driel, H. M. *Nature* **2000**, *405*, 437–440.
(9) Manners, I. *Science* **2001**, *294*, 1664–1666.
(10) Ni, Y.; Rulkens, R.; Manners, I. *J. Am. Chem. Soc.* **1996**, *118*, 4102–4114.
(11) Arsenault, A. C.; Miguez, H.; Kitaev, V.; Ozin, G. A.; Manners, I. *Adv. Mater.* **2003**, *15*, 503–506.
(12) MacLachlan, M. J.; Ginzburg, M.; Coombs, N.; Coyle, T. W.; Raju, N. P.; Greedan, J. E.; Ozin, G. A.; Manners, I. *Science* **2000**, *287*, 1460–1463.
(13) Lastella, S.; Jung, Y. J.; Yang, H.; Vajtai, R.; Ajayan, P. M.; Ryu, C. Y.; Rider, D. A.; Manners, I. *J. Mater. Chem.* **2004**, *14*, 1791–1794.
(14) Miguez, H.; Tétreault, N.; Hatton, B.; Yang, S. M.; Perovic, D.; Ozin, G. A. *Chem. Commun.* **2002**, 2736–2737.
(15) Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. *Chem. Mater.* **1999**, *11*, 2132–2140.
(16) Kim, S. H.; Misner, M. J.; Russell, T. P. *Adv. Mater.* **2004**, *16*, 2119–2123.
(17) Rider, D. A.; Power-Billard, K. N.; Cavicchi, K. A.; Russell, T. P.; Manners, I. *Macromolecules*, in press.
(18) Walton, D. G.; Kellogg, G. J.; Mayes, A. M.; Lambooy, P.; Russell, T. P. *Macromolecules* **1994**, *27*, 6225–6228.

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