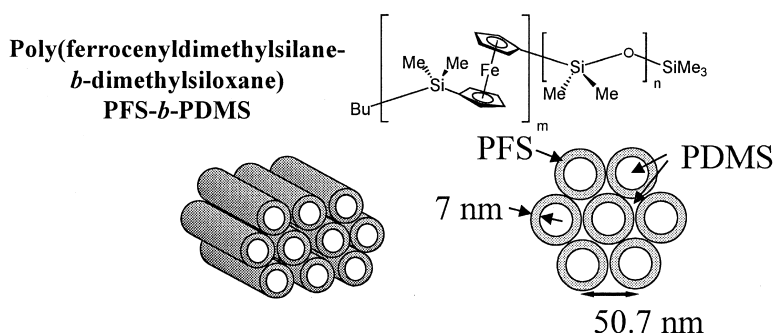Communication

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Bulk Microphase Segregation of an Asymmetric Organometallic-Inorganic Diblock Copolymer: A Remarkable Example of Concentric Cylinders

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Block copolymers self-assemble in the bulk state to form ordered arrays of nanostructures derived from the immiscible blocks.[1] These periodic assemblies are of intense current interest for the creation of nanostructured materials such as porous membranes, lithographic templates, reaction vessels, and photonic band gap materials.[1,2] A-*b*-B diblock copolymers in which each block comprises an amorphous polymer have been extensively studied. By varying the volume fraction of each block, one can generate a range of different morphologies in the strong segregation limit.[3] These consist of domains of the minor block, such as spheres, cylinders, or gyroids, within a continuous phase comprising the major component. As the asymmetry of the block copolymer increases, the curvature of the interface between the blocks will also increase. However, the curvature increase will be counterbalanced by the chain stretching/packing to fill any unoccupied volume inside both domains. Chain stretching depends on factors such as temperature, the degree of polymerization of each block, and the Kuhn length of the monomer.[4] For all of the cases of which we are aware, the longer block forms the continuous phase, whereas the shorter block forms the imbedded structures. In this communication, we report the remarkable formation of a self-assembled structure in which the shorter block forms cylindrical shells surrounding cylindrical domains formed by the longer block.

Polyferrocenylsilane block copolymers are of interest as the organometallic block is semiconducting and is a magnetic ceramic precursor, which offers intriguing possibilities for the generation of self-assembled materials with novel properties.[5] We have recently shown that asymmetric examples of the organometallic-inorganic diblock copolymer poly(ferrocenyl-dimethylsilane-*b*-dimethylsiloxane) (PFS-*b*-PDMS) form fascinating anisotropic micellar structures when dissolved in a selective solvent for the longer PDMS block.[6] This unusual behavior has been attributed to the crystalline nature of the PFS block.[7] Here we report on the microphase segregation of asymmetric PFS-*b*-PDMS samples in the bulk.

PFS-*b*-PDMS

A PFS$_{90}$-*b*-PDMS$_{900}$ sample (PDI = 1.01, volume fraction for PFS = 0.20) was synthesized via sequential anionic ring-opening polymerization.[6] Films of PFS$_{90}$-*b*-PDMS$_{900}$ of ca. 1 mm thickness

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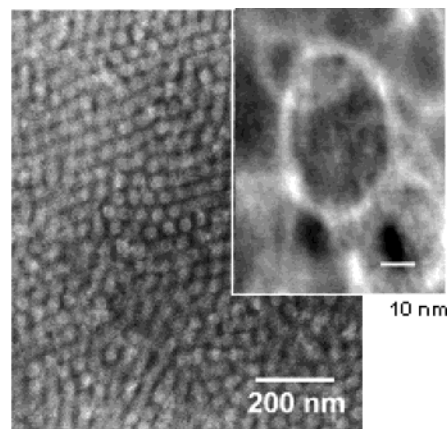[§] Materials Center Leoben.
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Figure 1. TEM micrograph of a cryomicrotomed PFS$_{90}$-*b*-PDMS$_{900}$ film cast from toluene. Inset: High-resolution STEM image of this sample obtained in the dark field mode.

were prepared by solvent casting from either toluene or THF (~20 mg/mL). The solvent was allowed to slowly evaporate in a closed container at room temperature. We viewed a cryomicrotomed sample of the film cast from toluene by conventional transmission electron microscopy (CTEM) in the bright field mode. Because the PFS block possesses electron-rich Fe atoms, unstained samples provide sufficient contrast between the PFS and PDMS blocks.[5,6] The TEM micrograph shows somewhat disordered hexagonal packed objects that are formed by the PDMS blocks (white areas), while the continuous phase appears gray (Figure 1). From the mean diameter of the PDMS circles (35.5 nm) and their lattice spacings (50.7 nm), we found that these circles occupy only 44% of the area of the hexagonal array, less than the 80% volume fraction of PDMS in the sample. The rest of the PDMS chains are located elsewhere.

To elucidate the morphology of the sample, we used scanning TEM (STEM) in the dark field mode to view an image of the electrons that are elastically scattered by the PFS domains. Figure 1 (inset) shows a STEM image where we see the presence of PFS rings (white) in the midst of the relatively electron-poor PDMS domains (black and gray). Electron energy loss measurements confirm the presence of Fe only in the 7 nm thick rings that surround the PDMS circles.

The small-angle X-ray scattering (SAXS) pattern of the film cast from toluene using a Cu Kα source shows broad peaks with relative positions of $3^{1/2}$, $7^{1/2}$, and $21^{1/2}$ (Figure 2, bottom). The broadness of the peaks represents the polydispersity in the sizes of the structures that can be observed in the TEM image. For hexagonal packed cylinders (Hex), the reflection peaks should have relative positions of $3^{1/2}$, $4^{1/2}$, $7^{1/2}$, $9^{1/2}$, $12^{1/2}$, $13^{1/2}$ ... not all of which would
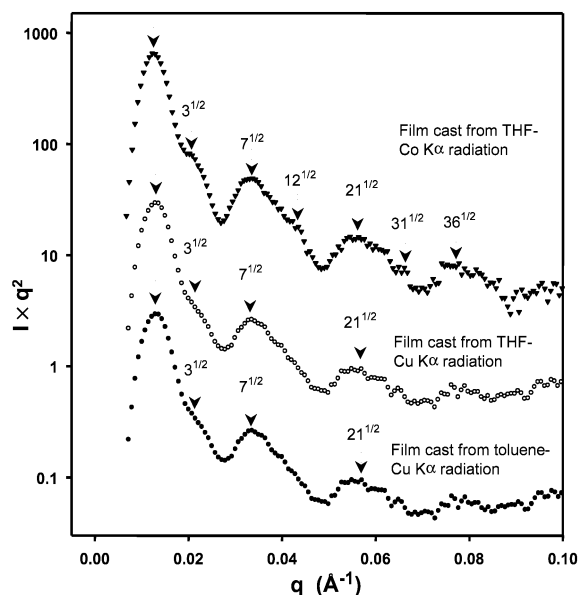
Figure 2. SAXS measurements (Bruker NanoSTAR system, 2D HI-STAR detector) of the PFS$_{90}$-b-PDMS$_{900}$ films cast from: (●) toluene, using Cu Kα radiation; (○) THF, using Cu Kα radiation; (▼) THF, using Co Kα radiation.

be observed. The SAXS pattern of the film cast from THF (Figure 2, center) shows the same reflections as that cast from toluene.

The presence of iron in the PFS block complicates the SAXS data as Fe fluoresces when it absorbs the Cu Kα radiation ($\lambda =$ 1.54 Å).[8] By using Co Kα radiation ($\lambda =$ 1.79 Å), we found that Fe fluorescence can be avoided. Figure 2 shows the SAXS pattern of a film cast from THF using Co Kα radiation. From the SAXS pattern, we can see better-resolved reflections with relative peak positions of $3^{1/2}$, $12^{1/2}$, $31^{1/2}$, and $36^{1/2}$. The relative positions of $31^{1/2}$ and $36^{1/2}$ correspond to the (5,1,0) and (6,0,0) Bragg peaks of Hex, respectively. The SAXS data indicate that we have hexagonal packed cylinders. Therefore, the PFS rings that we see in Figure 1 (inset) are actually shells surrounding the cylinders formed by the longer PDMS chains, and the remaining fraction of the PDMS fills the spaces between the cylinders.

Although we see small differences in peak resolution by using the two different radiation sources, the *d*-spacings are similar ($d =$ 55.1 and 54.1 nm for Cu and Co radiation, respectively). These lattice spacings are in agreement with the values measured by CTEM.

The reason for the formation of this novel kind of morphology by PFS$_{90}$-b-PDMS$_{900}$, where the minor block forms a concentric shell, is unclear. Indeed, previous studies of organometallic-organic PFS block copolymers have demonstrated the formation of classical bulk-phase morphologies, such as PFS spheres and cylindrical domains from asymmetric poly(styrene-*b*-ferrocenyldimethylsilane) (PS-*b*-PFS) with a longer, glassy PS block.[5,9] One possible explanation, that the conformationally flexible PDMS allows the PFS block to crystallize,[7] was ruled out by wide-angle X-ray scattering (WAXS) measurements. Thus, WAXS patterns of films cast from either toluene or THF revealed that both domains were

amorphous, a conclusion further supported by DSC measurements. Another possible explanation asserts that the combination of a relatively stiff PFS block with a highly flexible PDMS block plays a key role.[10] Although the Kuhn length (l_κ) of bulk PFS in a homopolymer film has not been determined, a value for l_κ between 1.53 and 2.12 nm was estimated by fitting SAXS data for PS-*b*-PFS to a model.[11] These values are substantially higher than that of PDMS ($l_\kappa = 0.56$ nm).[12] Because PFS is considerably stiffer than PDMS, we tentatively propose that it may be thermodynamically favorable for PFS to minimize its curvature along the interface by forming cylindrical shells. In contrast, the highly flexible PDMS chains may prefer to form the interior of the cylinders, as the curvature is higher.

In summary, we have shown that when an asymmetric PFS$_{90}$-b-PDMS$_{900}$ copolymer undergoes phase segregation, the longer block forms cylinders surrounded by a shell of PFS, with the remaining PDMS filling the interstitial spaces. Future work will focus on understanding this remarkable behavior.

Supporting Information Available: Experimental details for (S)-TEM, SAXS, and WAXS measurements and a schematic sketch of the morphology (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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