

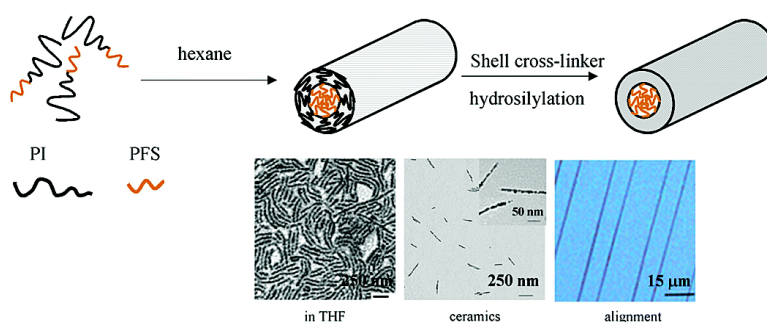
Communication

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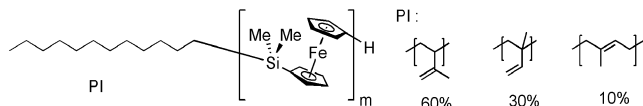
Shell Cross-Linked Cylinders of Polyisoprene-*b*-ferrocenyldimethylsilane: Formation of Magnetic Ceramic Replicas and Microfluidic Channel Alignment and Patterning

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In selective solvents, diblock copolymers can form micellar aggregates with the insoluble block as the core and the soluble block as the corona.^{1,2} In an important recent development, several groups have demonstrated that block copolymer micelles can be given a permanent shape by cross-linking of the core³ or the corona.⁴ Core or shell cross-linked spherical micelles are of considerable interest⁵ as nanospheres and nanocages.⁶ Studies of other morphologies are more rare, but cylindrical micelles formed from a triblock copolymer have been transformed into nanotubes^{7,8} by performing cross-linking of the central block followed by selective core degradation. In this communication we report the controlled, metal-catalyzed shell cross-linking of cylindrical micelles of the organic-organometallic diblock copolymer, polyisoprene-*b*-ferrocenyldimethylsilane (PI-*b*-PFS). This results in novel permanent cylindrical organometallic nanostructures with tunable dimensions, which allow the formation of PFS-derived arrays of size- and separation-controlled magnetic nanoclusters upon pyrolysis as well as microfluidic channel-assisted alignment and patterning.



As part of our continuing research on the self-assembly of polyferrocene-based block copolymers,⁹ PI₃₂₀-*b*-PFS₅₃ ($M_n = 30\,700$, PDI = 1.05) was prepared by sequential living anionic polymerization of isoprene and [1]dimethylsilaferrocenophane as previously described.¹⁰ Self-assembly of PI₃₂₀-*b*-PFS₅₃ in hexanes, a selective solvent for the PI block, yielded cylinders with a PFS core and PI corona.¹⁰

Shell cross-linking was performed by derivatizing the pendent vinyl groups on the coronal PI chains by means of Pt-catalyzed hydrosilylation chemistry. The cross-linker used was tetramethyldisiloxane, and the reaction was carried out in the presence of Karstedt's catalyst (PI₃₂₀-*b*-PFS₅₃ 1 mg/mL, 1 equiv of cross-linker per PI double bond, 4 d, 23 °C).¹¹ The absence of appreciable undesired intermicellar cross-linking was indicated by dynamic light scattering (DLS) measurements on the cross-linked micelles in hexane, which gave an apparent hydrodynamic radius, R_h , of 50 nm,¹² identical to that for uncross-linked micelles in the same solvent. TEM analysis of the cross-linked cylinders (Figure 1a) gave a core diameter of 20 nm and lengths of 50–400 nm,¹³ values which also resembled those for the uncross-linked analogues.

The stability of the cylinders was demonstrated by transferring the cross-linked micelles from hexanes to THF, a common solvent for both blocks. DLS analysis in THF gave an R_h value of 59 nm¹² which suggested the preservation of the cylindrical structure rather than dissociation to yield unimers, a conclusion confirmed by TEM (Figure 1b).¹³ ¹H NMR analysis in C₆D₆, also a common solvent

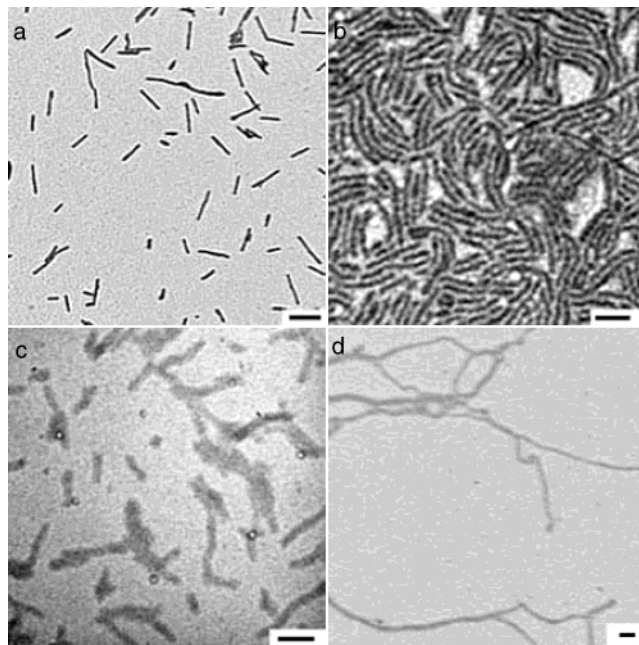


Figure 1. TEM micrographs for shell cross-linked cylindrical micelles derived from PI₃₂₀-*b*-PFS₅₃ (a) from hexane (b) from THF, (c) lightly cross-linked micelles from THF (d) cross-linked fibers from THF. All scale bars represent 250 nm.

for both blocks, was used to analyze the degree of cross-linking. The integration ratio between the resonance due to double bonds (4.8–6.1 ppm) and that for the ferrocene units (4.1–4.4 ppm) was calculated and compared before and after shell cross-linking. On the basis of this comparison, ca. 36% of the double bonds were consumed.

The moderate degree of cross-linking resulted in a degree of swelling (DOS) of 18% as indicated by the increase in R_h upon changing solvent from hexane to THF.¹¹ The DOS of PI₃₂₀-*b*-PFS₅₃ could be conveniently controlled by adjusting the quantity of the disiloxane cross-linker. For example, lowering the quantity of tetramethyldisiloxane to 0.15 equiv per PI double bond in the hydrosilylation reaction led to complete consumption of the Si–H groups after 14 d by IR analysis.¹¹ In this case the R_h value for the cross-linked aggregates in THF was found to be 76 nm, which corresponds to a DOS of 52%. The larger value for the DOS was apparent from TEM analysis (Figure 1c) where micelles with widths up to 45 nm were observed, a value more than twice that for the original uncross-linked cylinders (20 nm). The shrinkage of these swollen cylinders back to their original width was achieved by slowly adding hexane to the THF solution.¹¹ In contrast, when the cross-linking reaction was performed with a large excess of disiloxane cross-linker (2 equiv per PI double bond, 2 d),¹¹ the

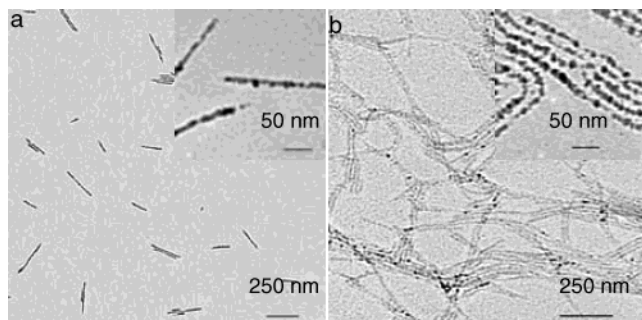


Figure 2. TEM micrographs for ceramics generated by the pyrolysis of PI₃₂₀-*b*-PFS₅₃ shell cross-linked cylindrical (a) micelles (DOS = 0%) and (b) fibers (DOS = 26%) aerosol sprayed from THF.

resulting shell cross-linked cylinders exhibited no detectable swelling by DLS upon transferring from hexane to THF. In addition, the signals for the PFS and PI blocks were extremely broad and were barely detectable by ¹H NMR due to the highly cross-linked network structure, with only the Me resonances being clearly defined.

By adjusting the hexane/THF ratio during the initial PI-*b*-PFS self-assembly process, the micelle dimensions could be varied from cylinders with lengths of 50–400 nm to fibers with lengths of > 10 μm.¹¹ Hydrosilylative cross-linking of PI-*b*-PFS fibers with a width of 20 nm and a length > 10 μm yielded permanent structures which retained their structural integrity in THF but which swelled to a width of 50 nm (see TEM Figure 1d).

The presence of metallic elements in polymer structures can introduce additional functionality.¹⁴ For example, pyrolysis of PFS homopolymers can yield magnetic ceramics containing iron nanoclusters dispersed within an amorphous C/SiC matrix.^{15,16} For high ceramic yields to be obtained, the use of a cross-linked PFS network is generally necessary.¹⁶ Accordingly, pyrolysis of uncross-linked PI₃₂₀-*b*-PFS₅₃ cylindrical micelles was found to lead to the destruction of the structure, as shown by TEM analysis. In striking contrast, shell cross-linked cylinders or fibers of PI₃₂₀-*b*-PFS₅₃ produced ceramics with excellent shape retention upon heating to 600 °C under N₂ (Figure 2).¹¹ This indicated that the shell cross-linking plays an essential role in shape retention and permits the formation of a ceramic replica.¹⁷ Fe nanoclusters with diameters of ca. 10–15 nm could be discerned by TEM, whose proximity was a function of the degree of cross-linking which can be indicated by the DOS. Thus, the Fe nanoclusters were closely packed when derived from highly cross-linked cylinders (DOS = 0%, Figure 2a inset), whereas clear separation was apparent in the case of more swollen materials (DOS = 26%, Figure 2b inset).¹¹ Pyrolysis temperature should be another key variable allowing us to adjust nanocluster size and the ensuing magnetic properties.¹⁵

We have also found that the stability of the shell cross-linked cylinders permits their use in microfluidic channel-assisted nanopatterning.¹⁸ The cross-linked cylinders dispersed in a 1:1 mixture of hexane/butanol were readily patterned by capillary forces inside poly(dimethylsiloxane) microchannels,¹¹ and this proved to be a promising method for micelle alignment. In the case of the relatively thick lines derived from a highly concentrated solution, which presumably consist of cylinder bundles, analysis was achieved by means of optical microscopy (Figure 3a). In contrast, the thinner lines derived from a more dilute solution were characterized by SEM (Figure 3b).

In summary, stable organometallic cylinders with tunable swellability have been created by cross-linking the shell of cylindrical micelles of PI₃₂₀-*b*-PFS₅₃ via metal-catalyzed hydro-

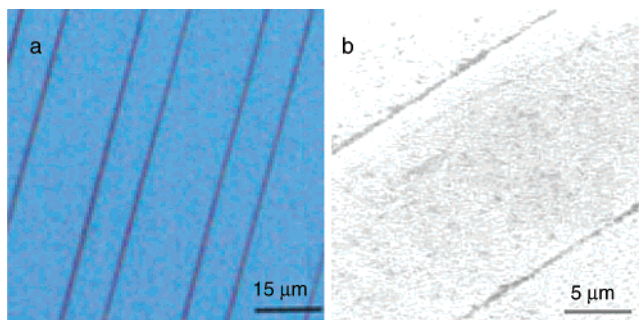


Figure 3. (a) Optical image and (b) SEM image for microfluidically aligned cross-linked PI₃₂₀-*b*-PFS₅₃ micelles.

silylation. The presence of a cross-linked corona was found to permit the pyrolysis-induced formation of cylindrical ceramic replicas containing size and separation tunable arrays of Fe nanoclusters. In addition, microfluidic alignment of the cross-linked cylinders was possible. Future work will target the generation of single-micelle lines and the formation of magnetic ceramic nanopatterns using this technique.

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Supporting Information Available: Experimental and characterization details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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