


Organometallic Nanotubes

**Swellable, Redox-Active Shell-Crosslinked
Organometallic Nanotubes**

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Carbon nanotubes have a range of remarkable properties and these fascinating structures now represent a key building block in nanoscience and technology.^[1] Since their discovery,^[2] the synthesis of analogous structures with other

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compositions has attracted much attention and a variety of inorganic nanotubes have also been described.^[3] Organic and organometallic nanotubes^[4] would further complement the available structures. However, relatively few successes have been reported in this area.

Block copolymers comprise chemically distinct but individually homogeneous polymer chains joined together end-to-end by covalent bonds. These molecules self-assemble in block-selective solvents into core–corona micellar nanostructures, in which the solvent-insoluble block forms the core and the solvent-soluble block forms the shell.^[5] Although a range of micellar morphology, including spheres, cylinders, vesicles, have been identified,^[6] nanotubes are rare.^[4g–j] We recently found that PFS–*b*–PDMS (PFS: polyferrocenylsilane, PDMS: polydimethylsilane) with a block ratio of 1:12 self-assembles either in hexane or in decane (solvents which are selective for PDMS) to form organometallic nanotubes with PFS as the inner wall and PDMS as the corona. From the fact that these tubes in hexane were able to entrap tetrabutyl lead, we imagine that the tube ends are open to solvent.^[7] However, the further exploration and utility of these fascinating nanomaterials, which should have interesting physical properties by virtue of the metal-containing PFS block,^[8,9] has been impeded by the instability of these self-assembled structures, which dissociate in solvent that is not selective for PDMS or at elevated temperature.

Core- and shell-crosslinking reactions have been developed as a technique to endow permanence to block copolymer micelles and to create additional opportunities for applications.^[10,11] For example, nanocages have been created from shell-crosslinked spherical micelles.^[12] We recently reported the self-assembly of PI–PFS (PI: polyisoprene) cylindrical micelles, which could be shell-crosslinked by metal-catalyzed hydrosilylation.^[13] The resulting permanent organometallic cylinders served as a precursor for ceramic nanolines upon pyrolysis and could be aligned on a flat substrate through a microfluidic template, thus providing an opportunity for the fabrication of nanopatterned arrays. Herein, we report the synthesis, self-assembly, and shell-crosslinking of PFS–PMVS (PMVS: polymethylvinylsiloxane), which leads to stable organometallic nanotubes that have redox activity and tunable swellability (Scheme 1).

The organometallic–inorganic block copolymer PFS₄₈–PMVS₃₀₀ (number average molecular weight (M_n) = 40700; polydispersity index (PDI) = 1.10, PFS:PMVS = 1:6) was

synthesized through sequential anionic polymerization in THF. The polymers self-assemble in hexane, a selective solvent for PMVS, to form nanotubes. As shown in Figure 1 a, the nanotubes appear as stiff hollow structures, with a mean

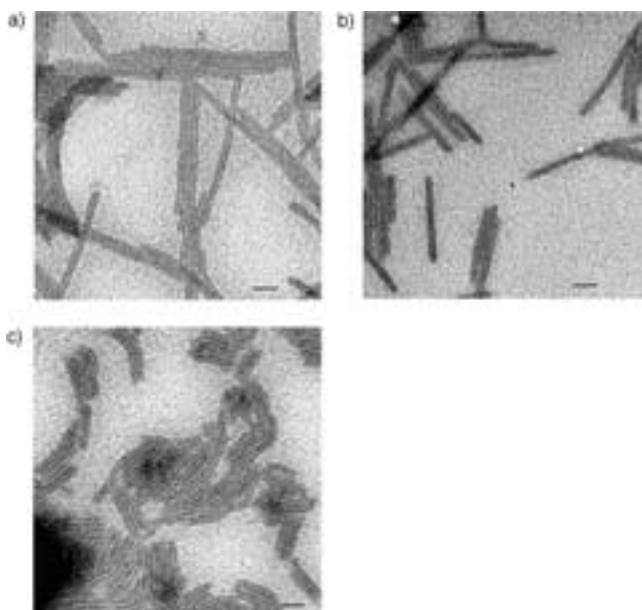
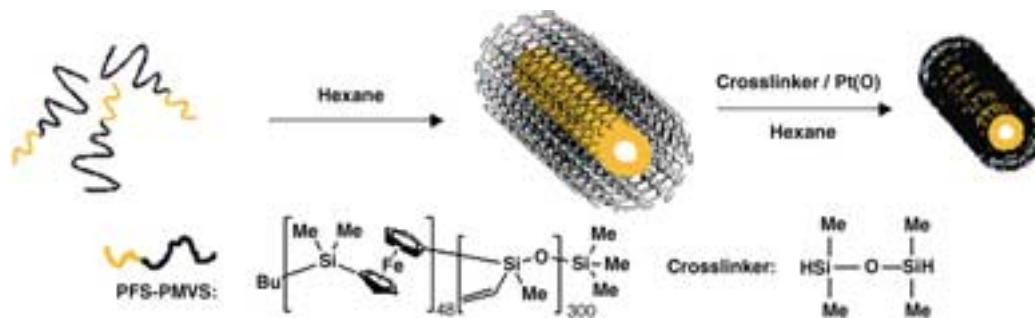


Figure 1. TEM images for the samples prepared from a) self-assembled PFS–PMVS nanotubes in hexane, b) shell-crosslinked nanotubes in hexane and c) in THF. Scale bar: 100 nm.

length of about 400 nm, and they have a cavity diameter of 8 nm and a PFS wall thickness of 8 nm.^[7,14]

Taking advantage of pendant vinyl groups in PMVS,^[13] we were able to crosslink the corona by using a metal-catalyzed hydrosilylation reaction with tetramethyldisiloxane. For example, a solution of PFS–PMVS nanotubes in hexane (1 mg mL^{−1}) was treated at room temperature for 3 days with tetramethyldisiloxane (0.5 equiv per vinyl group) in the presence of Karstedt's catalyst. Dynamic light scattering (DLS) measurements are useful for monitoring changes in micelle size. These measurements showed that the apparent hydrodynamic radius, R_h , of 85 nm for uncrosslinked micelles was reduced to 69 nm for the crosslinked micelles. The reduction in R_h indicates that the micelle corona is less swollen by solvent at this level of crosslinking. In the TEM



Scheme 1. Synthesis of stable organometallic nanotubes.

images, however (see Figure 1 b) the structures appear to be very similar.^[15]

A more important test of the influence of crosslinking is to examine the consequences of exposing the nanotubular structures shown in Figure 1 b to a common solvent for both blocks such as benzene, toluene, or tetrahydrofuran (THF). For the uncrosslinked PFS-*b*-PMVS nanotubes (Figure 1 a), exposure to these solvents led to a solution of unimers. In contrast, the crosslinked nanotubes maintained their size. DLS measurements on this sample in THF gave an R_h value of 67 nm, similar to the value of 69 nm for the value in hexane. ^1H NMR spectroscopic analysis in C_6D_6 allowed the reaction of the pendant vinyl groups of the PMVS chains to be monitored. After shell-crosslinking, it became barely possible to observe the signals due to vinyl groups, which suggests that most were consumed and that a high degree of crosslinking occurred.

A droplet of the crosslinked micelle solution in THF was placed on a TEM grid and, after solvent evaporation, gave images such as that shown in Figure 1 c. The structures formed are similar in contour length to those seen in Figure 1 b. They appear to be hollow, but much more flexible. The overall width of the core of the tubes is expanded slightly from a value of 25 nm for tubes formed in hexane to 30 nm for the sample formed as the THF evaporates on the TEM grid. Another difference between this structure and that of the initially crosslinked nanotubes in hexane is the nature of the PFS domains. Films formed from the nanotubes in hexane, both before and after the crosslinking reaction, exhibit a strong peak in the wide-angle X-ray scattering (WAXS) spectrum with a d spacing of 6.3 Å, characteristic of the distance between adjacent planes in crystalline PFS.^[16,17] In contrast, no peaks were seen in the WAXS spectrum of films formed from a THF solution of the crosslinked structures.^[17] These films yielded only an amorphous halo. The flexibility of the structures seen in Figure 1 c may be related to the amorphous nature of the PFS domains, as amorphous structures have a lower degree of rigidity than crystalline analogues.

Another test of the stability of a self-assembled structure is its stability upon exposure to ultrasound. We previously reported that the cylindrical micelles formed from PFS₅₀-PDMS₃₀₀ underwent irreversible fragmentation to form shorter, stubbier cylinders of similar width when a hexane solution of the micelles was placed in a 60 w ultrasonic cleaning bath.^[18] The process was followed by DLS. Here we found similar results. A solution of the uncrosslinked nanotubes in hexane underwent eventual degradation when placed in a 60 w ultrasonic bath. Over 25 min of sonication, R_h decreased from about 85 nm to less than 50 nm. Shorter tubelike structures were observed by TEM, and the smaller structures did not grow in size (DLS, TEM) when the hexane solution was allowed to stand undisturbed for 3 days at 23°C. In contrast, the R_h of the crosslinked structures, under the same set of sonication conditions, remained constant at 67 nm (Figure 2).

The success of the crosslinking reaction opens the way for new experiments in which the nature and the extent of crosslinking can be varied. For example, one can choose a

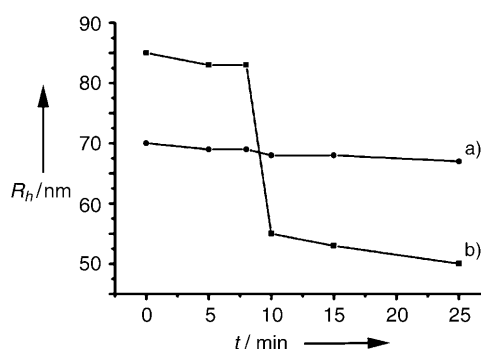


Figure 2. R_h as a function of sonication time for a) crosslinked micelles and b) uncrosslinked micelles.

different siloxane-based crosslinker with a longer spacer between the reactive Si-H groups. We carried out a series of reactions with hydride-terminated polydimethylsiloxane (H-PDMS-H, $\bar{M}_n = 400$ –500, 0.5 wt % H). The TEM images of the resulting shell-crosslinked micelles deposited from hexane (Figure 3 a) appear identical to those crosslinked by

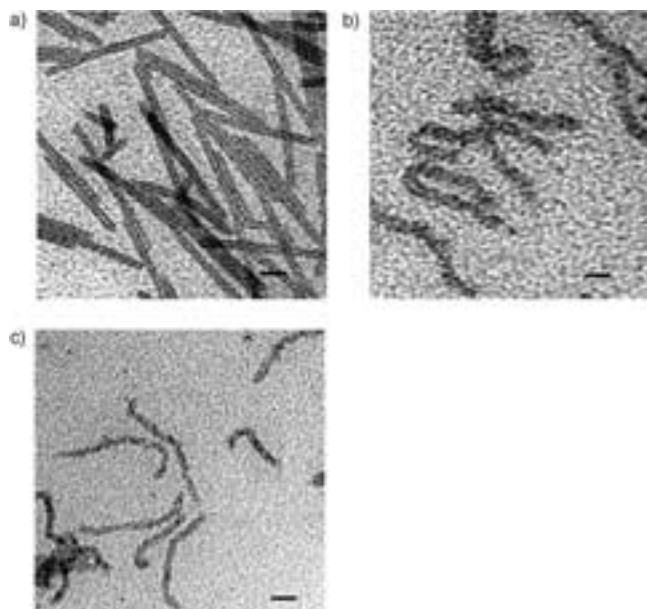


Figure 3. TEM images for shell crosslinked micelles with hydride-terminated polydimethyl siloxane, $\bar{M}_n = 400$, as crosslinker. a) Sample prepared from crosslinked micelles in hexane, b) from crosslinked micelles in toluene, and c) from crosslinked micelles in toluene/hexane mixture (1:3 by volume). Scale bar: 100 nm.

tetramethyldisiloxane (see Figure 1 b). Differences appear in the TEM images of these structures when they are spread on the TEM grid from toluene, a common solvent in which both blocks are soluble. As seen in Figure 3 b, the structures are not only less rigid but also wider. Their width is about 55 nm, which is more than twice that of original micelles formed in hexane (25 nm).

To help us understand the origin of this increase in tube diameter for structures seen in the TEM images, we carried

out additional experiments in which we slowly added hexane to the toluene solution of the nanotubes crosslinked with H-PDMS-H. Remarkably, the “swollen” shell-crosslinked tubes seen in Figure 3b gradually decreased in thickness back towards their original size. As shown in Figure 3c, TEM samples prepared from a solution containing a 3:1 mixture by volume of hexane to toluene had a PFS core width of 27 nm. In addition, these structures no longer appear to be hollow. They more closely resemble dense cylinders. Thus, the TEM images of these structures are sensitive to the state of the crosslinked structures in solution. In samples formed in pure toluene, both polymer blocks are swollen by the common solvent, and phase separation probably occurs on the TEM grid as the solvent evaporates. When hexane is added to the solution, it promotes selective precipitation of the PFS chains to form domains of nanometer dimensions, whose size is limited by the connectivity of the PFS to the crosslinked PMVS corona. Hexane evaporates more rapidly than toluene, and the final structures seen in Figure 3c are likely to be related in a complex way to the composition of the medium as the sample dried.

Crosslinked structures of nanometer dimensions swollen by solvent are often referred to as “microgel” particles. The crosslinked nanotubes “dissolved” in a common suitable solvent are two-component microgels, in which the PFS chains dangle from the network of PMVS chains. The stability of these structures in a common solvent for both blocks makes it possible to characterize their electrochemical behavior by cyclic voltammetry (CV). The experiments, on samples crosslinked with tetramethyldisiloxane, were carried out in a mixture of dichloromethane and benzonitrile (2:1 by volume) that contained 0.1 M $[\text{NBu}_4][\text{PF}_6]$ as the supporting electrolyte. For comparison, CV experiments were also carried out on the uncrosslinked block copolymers. Under these conditions, the polymers exist as unimers as characterized by DLS. As shown in Figure 4a, the PMVS network of the microgel particles does not prevent electron transfer involving the redox-active PFS component. Two reversible oxidation waves for the PFS chains were observed which, based on studies of PFS homopolymer, is characteristic of the presence of interacting metal centers.^[19] In fact, the protection afforded by the PMVS network appears to prevent the deposition of oxidized micelles on the electrode surface, as suggested by the presence of a relative smooth reduction curve. In contrast, the uncrosslinked block copolymers exhibit a sharp peak upon reduction (Figure 4b), characteristic of the precipitation of oxidized PFS chains on the electrode surface.^[19]

In summary, PFS-*b*-PMVS block copolymers, synthesized by anionic polymerization, underwent self-assembly in hexane to form organometallic nanotubes. The PMVS shell could be crosslinked in hexane, thus preserving the structure but leading to a contraction of the corona dimensions. These crosslinked micelles formed stable redox-active microgel particles in a common suitable solvent, and these particles swell or shrink depending on the solvent composition. The degree of swelling was dictated by the molecular weight of the crosslinker. These properties may render these nanotubes useful building blocks for a variety of applications.

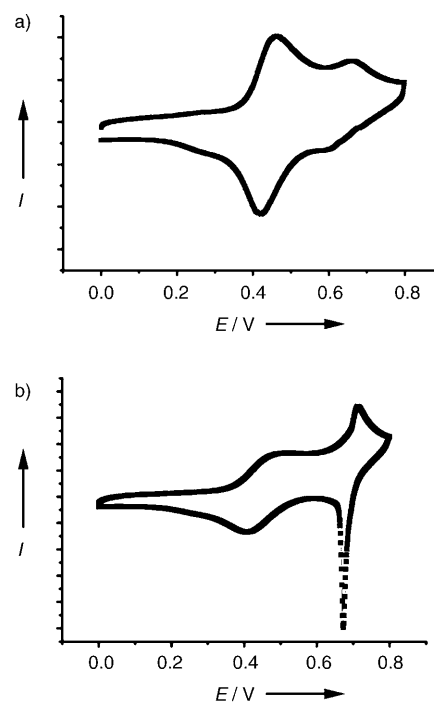


Figure 4. Cyclic voltammetry of a) crosslinked nanotubes and b) PFS-PMVS block copolymer in dichloromethane/benzonitrile (2:1) with 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte.

Experimental Section

Synthesis of PFS-PMVS: In an N_2 -filled glovebox at room temperature, *n*BuLi (1.6 M; 60 μL , 9.6×10^{-5} mol) in hexanes was added quickly to a stirred solution of [1]silaferrocenophane (1.18 g, 4.8×10^{-3} mol) in THF (10 mL). After 40 min, the solution changed from a red to a deep amber color, and then 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (2.90 g, 11.60×10^{-3} mol) was added to the solution of living polymer along with a few drops of [12]crown-4. The reaction flask was immediately removed from the glovebox and placed on a Schlenk line under prepurified Ar and cooled to 0 °C. The reaction proceeded for 20 h at 0 °C and was terminated by the addition of a few drops of Me_3SiCl . The block copolymer was precipitated into methanol (ca. 500 mL) in the presence of triethylamine (ca. 10 mL), isolated, and washed with hexane to remove side products, followed by drying under vacuum for 24 h, yielding 3.8 g of the amber gummy product (yield = 93 %). ^1H NMR (300 MHz, C_6D_6) data: δ = 0.50 (s, $[\eta\text{-C}_5\text{H}_4]_2\text{FeSiMe}_2$), 4.10 (s, Cp), 4.26 (s, Cp), and 0.28 (s, $[\text{MeSiO}]_3$), 5.80–6.40 ppm (m, $[\text{CH}_2=\text{CH-SiO}]_3$). GPC: M_n (PDI): 11 700 (1.02) for the PFS block, and 40 700 (1.10) for the PFS-PMVS diblock copolymer.

Self-Assembly of PFS-PMVS and Shell-crosslinking Reaction: Instrumentation and characterization: Molecular weight and molecular-weight distribution was characterized by gel permeation chromatography (GPC) by using a Waters Associates 2690 Separations Module equipped with Ultrastaygel columns with pore sizes of 10^3 – 10^5 Å, in-line degasser, and a differential refractometer. The ^1H NMR spectra were recorded on a Varian Gemini 300 spectrometer with deuterated benzene as solvent. DLS experiments were carried out by using AVL-5000 operating in the dynamic mode. Cumulant fitting of autocorrelation functions provide hydrodynamic radii with an error of ± 0.1 nm and no model was used. WAXS samples were prepared by casting a film from PFS-PMVS hexane solution on an aluminum substrate. Transmission electron microscopy (TEM) measurements were carried out with an Hitachi model 600 electron microscope operating at 75 kV. The samples were prepared by drying a drop of

the micelle solution on a carbon-coated copper grid. Iron-containing PFS chains provide electron-rich domains, which furnished the contrast for imaging self-assembled nanostructures.

Micellization: Tubelike micelles were prepared by mixing PFS-PMVS with hexane at 50–60 °C with stirring for 1 hour before cooling to room temperature. An aliquot was taken for light scattering and TEM experiments.

Shell crosslinking: A typical hydrosilylation shell-crosslinking reaction was performed as follows: Tetramethylsiloxane (7 μ L, 1.2×10^{-4} mmol) and Karstedt's catalyst (7 μ L) were added to a PFS-PMVS hexane micelle solution (10 mg/10 mL; vinyl group content: 2.4×10^{-4} mmol) at room temperature with stirring. At the end of the reaction, the solution was passed through an aluminum oxide column to remove the metal catalyst to yield a clear yellow solution of micelles. An aliquot of the hexane solution was used for DLS and TEM analysis. Then the hexane was removed by a flow of air to recover solid crosslinked micelles, which were redispersed in THF. DLS and TEM analyses of the shell crosslinked micelles in THF solution were carried out as described above directly without filtration.

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- [1] R. C. Haddon, *Acc. Chem. Res.* **2002**, *35*, a special issue on nanotube science.
- [2] S. Iijima, *Nature* **1991**, *354*, 56–58.
- [3] C. N. R. Rao, M. Nath, *Dalton Trans.* **2003**, 1–24.
- [4] a) D. T. Bong, T. D. Clark, J. R. Granja, M. R. Ghadiri, *Angew. Chem.* **2001**, *113*, 1016–1041; *Angew. Chem. Int. Ed.* **2001**, *40*, 988–1011; b) M. R. Ghadiri, J. R. Granja, R. A. Milligan, D. E. Mcree, N. Khazanovich, *Nature* **1993**, *366*, 324–327; c) M. Reches, E. Gazit, *Science* **2003**, *300*, 625–627; d) S. F. Ai, G. Lu, Q. He, J. B. Li, *J. Am. Chem. Soc.* **2003**, *125*, 11140–11141; e) Y. Kim, M. F. Mayer, S. C. Zimmerman, *Angew. Chem.* **2003**, *115*, 1153–1158; *Angew. Chem. Int. Ed.* **2003**, *42*, 1121–1126; For macroscopic tubes see: f) D. Y. Yan, Y. F. Zhou, J. Hou, *Science* **2004**, *303*, 65–67; Nanotubes from block copolymers: g) S. Stewart, G. Liu, *Angew. Chem.* **2000**, *112*, 348–352; *Angew. Chem. Int. Ed.* **2000**, *39*, 340–344; h) R. Mäki-Ontto, K. de Moel, W. de Odorico, J. Ruokolainen, M. Stamm, G. ten Brinke, O. Ikkala, *Adv. Mater.* **2001**, *13*, 117–121; i) K. Yu, A. Eisenberg, *Macromolecules* **1998**, *31*, 3509–3518; j) S. Rosselli, A.-D. Ramminger, T. Wagner, B. Silier, S. Wiegand, W. Häußler, G. Lieser, V. Scheumann, S. Höger, *Angew. Chem.* **2001**, *113*, 3233–3237; *Angew. Chem. Int. Ed.* **2001**, *40*, 3137–3141.
- [5] a) A. Halperin, M. Tirrell, T. P. Lodge, *Adv. Polym. Sci.* **1992**, *100*, 31–71; b) S. Förster, M. Antonietti, *Adv. Mater.* **1998**, *10*, 195–217; c) A. Choucair, A. Eisenberg, *Eur. Phys. J. E* **2003**, *10*, 37–44.
- [6] a) L. Zhang, A. Eisenberg, *Science* **1995**, *268*, 1728–1731; b) S. Jain, F. S. Bates, *Science* **2003**, *300*, 460–464; c) D. E. Discher, A. Eisenberg, *Science* **2002**, *297*, 967–973; d) S. A. Jenekhe, X. L. Chen, *Science* **1998**, *279*, 1903–1907; e) Z. L. Zhou, Z. B. Li, Y. Ren, M. A. Hillmyer, T. P. Lodge, *J. Am. Chem. Soc.* **2003**, *125*, 10182–10183; f) J. F. Gohy, N. Willet, S. Varshney, J. X. Zhang, R. Jerome, *Angew. Chem.* **2001**, *113*, 3314–3316; *Angew. Chem. Int. Ed.* **2001**, *40*, 3214–3216; j) Y. F. Liu, V. Abetz, A. H. E. Müller, *Macromolecules* **2003**, *36*, 7894–7898.
- [7] For detailed characterization of PFS block copolymer nanotubes see: J. Raetz, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **2002**, *124*, 10381–10395.
- [8] a) I. Manners, *Science* **2001**, *294*, 1664–1666; b) J. A. Massey, M. A. Winnik, I. Manners, Z. H. V. Chan, J. M. Ostermann, R. Enchelmaier, J. P. Spatz, M. Möller, *J. Am. Chem. Soc.* **2001**, *123*, 3147–3148; c) K. Kulbaba, I. Manners, *Macromol. Rapid Commun.* **2001**, *22*, 711–724.
- [9] For recent work on the solution self-assembly of metal-containing block copolymers see: a) J.-F. Gohy, B. G. G. Lohmeijer, S. K. Varshney, U. S. Schubert, *Macromolecules* **2002**, *35*, 7427–7435; b) S. Hou, K. Y. K. Man, W. K. Chan, *Langmuir* **2003**, *19*, 2485–2490.
- [10] For core crosslinking reactions: a) A. Guo, G. Liu, J. Tao, *Macromolecules* **1996**, *29*, 2487–2493; b) F. Henselwood, G. Liu, *Macromolecules* **1998**, *31*, 4213–4217; c) Y. Won, H. T. Davis, F. S. Bates, *Science* **1999**, *283*, 960–963.
- [11] For shell-crosslinking reactions: a) K. B. Thurmond, T. Kowalewski, K. L. Wooley, *J. Am. Chem. Soc.* **1996**, *118*, 7239–7240; b) K. B. Thurmond, T. Kowalewski, K. L. Wooley, *J. Am. Chem. Soc.* **1997**, *119*, 6656–6665; c) J. Ding, G. Liu, *Macromolecules* **1998**, *31*, 6554–6558; d) V. Bütün, A. B. Lowe, N. C. Billingham, S. P. Armes, *J. Am. Chem. Soc.* **1999**, *121*, 4288–4289.
- [12] a) G. J. Liu, *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 200–208; b) K. L. Wooley, *Chem. Eur. J.* **1997**, *3*, 1397–1399.
- [13] X. S. Wang, A. Arsenault, G. A. Ozin, M. A. Winnik, I. Manners, *J. Am. Chem. Soc.* **2003**, *125*, 12686–12687.
- [14] The block ratio appears to have little effect on the morphologies of the micelles. For example, PFS-PMVS block copolymers with block ratio of 1:10 also self-assemble into nanotubes. X. S. Wang, M. A. Winnik, I. Manners, unpublished results.
- [15] Only the PFS inner wall is visible in TEM, corona chains are invisible due to their comparatively low electron density.
- [16] J. A. Massey, K. Temple, L. Cao, Y. Rharbi, J. Raetz, M. A. Winnik, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 11577–11584; b) V. S. Papkov, M. V. Gerasimov, I. I. Dubovik, S. Sharma, V. V. Dementiev, K. H. Pannell, *Macromolecules* **2000**, *33*, 7107–7115.
- [17] see supporting information for further details.
- [18] J. Massey, K. N. Power, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **1998**, *120*, 9533–9540.
- [19] a) D. A. Foucher, J. M. Nelson, C. Honeyman, B. Z. Tang, I. Manners, *Angew. Chem.* **1993**, *105*, 1843–1845; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1709–1711; b) R. Rulkens, A. J. Lough, I. Manners, S. R. Lovelace, C. Grant, W. E. Geiger, *J. Am. Chem. Soc.* **1996**, *118*, 12683–12695.