



	Experiment title: Shape-Controlled Nanoparticle Synthesis Through Hierarchical Self-Assembly of Block Copolymer-Amphiphile Systems	Experiment number: SC-2530
Beamline: ID02	Date of experiment: from: Nov. 28, 2008 to: Dec. 1, 2008	Date of report: Aug. 24, 2009
Shifts: 9	Local contact(s): Dr. Michael SZTUCKI	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): * Roy Shenhar, Institute of Chemistry, The Hebrew University of Jerusalem * Uri Raviv, Institute of Chemistry, The Hebrew University of Jerusalem * Inbal Davidi, Institute of Chemistry, The Hebrew University of Jerusalem * Mariela Pavan, Institute of Chemistry, The Hebrew University of Jerusalem		

Report:

The target of the research project under which the experiment at ID02 was performed is to provide a self-assembly approach for the synthesis of anisotropic nanoparticles and nanoparticle aggregates. The approach is based on the formation of hierarchical structures based on block copolymer and amphiphile molecules, which feature anisotropic concentrations of metal precursors. These precursors are introduced either directly by an organometallic amphiphile or indirectly by loading a pre-formed hierarchical structure with metal salts. A subsequent reduction step affords nanoparticles.

The aim of the experiment at ID02 was to provide structural data on the hierarchical assemblies obtained before and after metal reduction, in order to support and complement preliminary evidence we have obtained from electron microscopy for the formation of anisotropic aggregates of nanoparticles that are periodically ordered in the nanocomposite. We have analyzed samples of four different polystyrene-*block*-poly(2- or 4-vinyl pyridine) (PS-P2VP or PS-P4VP) copolymers of various molecular weights (M_n 37, 50, 63, and 199 kDa), which were combined with three different amphiphiles (the organometallic amphiphiles palladium-pincer complex Pd-SCS and $Zn(DBS)_2$ [zinc dodecabenzesulfonate], and the organic amphiphile PDP [pentadecylphenol]) at various amphiphile:pyridine ratios (usually in the range of 0.5-1.0 pyridine equivalents). To study the effect of reduction on the nanocomposite structures, another set of relaxed composites containing the Pd-SCS amphiphiles were reduced with $NaBH_4$ in different solvent systems for different periods of time (in the range of 1-10 days). Analogously, samples containing the $Zn(DBS)_2$ were reacted with HF in an attempt to generate semiconductor ZnF nanoparticles, and samples containing the PDP amphiphile were repeatedly loaded with different metal salts ($AgNO_3$, $CoCl_2$, $NiCl_2$, $FeCl_2$, $FeCl_3$, and $Cu(OAc)_2$) and reduced (up to 3 cycles), in order to probe the possibility to selective load metal precursors into the appropriate locations in the hierarchical structure and to generate nanoparticles from them. Wide angle camera was used to characterize the formed inorganic nanocrystals.

Figure 1 shows typical scattering curves of PS-P2VP 199 kDa with Pd-SCS (0.9 equiv.) before and after reduction with $NaBH_4$. Before reduction (green curves), the small angle region reveals the formation of both a lamellar structure with 62.2 nm period and a finer structure with 3.4 nm period (evidenced by a broad peak at $q = 1.84 \text{ nm}^{-1}$). An additional sharp peak at $q = 2.7 \text{ nm}^{-1}$ indicates the formation of a periodic structure with a 2.3 nm repeat distance.

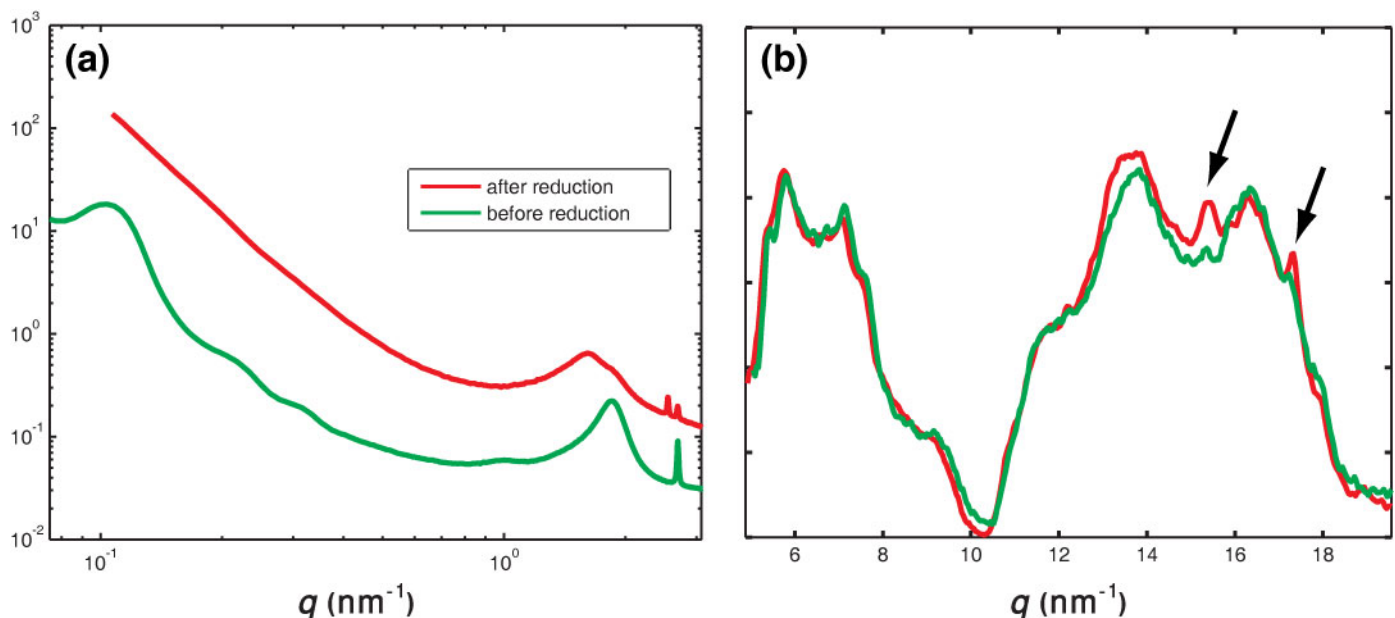


Figure 1. (a) SAXS and (b) WAXS curves of PS-P2VP 199 kDa with Pd-SCS (0.9 equiv.) before and after reduction with NaBH_4 in 1:1 water/methanol for 7 days.

The 62.2 nm period corresponds to the periodicity of the alternating PS-P2VP lamellae in the microphase separated structure. However, this repeat distance is considerably reduced compared to that of the pure block copolymer (75.0 nm). This issue will be addressed below. The broad peak is attributed to the formation of periodic sub-domains inside the P2VP domains, induced by the phase separation of the Pd-SCS amphiphile molecules bound to the pyridine groups on the polymer chain. The 3.4 nm repeat distance corresponds to the length of two Pd-SCS amphiphiles augmented by the effective thickness of the P2VP chain. An analogous broad peak was observed also for the PS-P2VP/PDP samples, which supports this assignment. However, the sharp peak at $q = 2.7 \text{ nm}^{-1}$ was only observed in the Pd-SCS samples, indicating the possible formation of pure phases of Pd-SCS amphiphiles that did not bind to the P2VP chains.

In the reduced sample (red curves), the small angle region becomes rather featureless (besides the peak at $q = 1.8 \text{ nm}^{-1}$, which indicates the preservation of the hierarchical structure), while the wide angle region reveals an increase in the relative intensity of a broad peak and a sharp peak (at $q = 15.4 \text{ nm}^{-1}$ and 17.3 nm^{-1} , corresponding to 4.1 and 3.6 Å periods, respectively, denoted in arrows in Figure 1). The location of the sharp peak corresponds to the atomic diameter of palladium atom (3.56 Å, according to the periodic table), and thus indicates the formation of Pd nanoparticles (in addition to the TEM analysis). We could not assign the broader peak as well as the rest of the WAXS data. Following transmission electron microscopy analyses of the samples performed after the experiment we conclude that the lack of information in the small angle region results from the heterogeneity of the reduced sample, caused by the impeded penetration of the NaBH_4 through the thick polymer matrix into deeper areas in the sample as well as swelling (and possible destruction) of the amphiphile-divided P2VP substructure in locations closer to the surface of the sample. We are currently developing alternative sample preparation techniques that would allow the fabrication of uniformly reduced samples with preserved hierarchical structures.

Similar results were obtained with the other block copolymer lengths. Probing the solvent effect on the reduction results indicated that no reduction occurred with water due to lack of penetration, extensive reduction (probably followed by the destruction of the hierarchical structure) occurred with methanol solutions (indicating efficient penetration), and more moderate extent of reduction was observed with 1:1 water:methanol solutions (which seems to be the optimal solvent composition). Reduction with H_2 (without a solvent) gave rise to a new, sharp diffraction peak corresponding to 2.4-2.5 nm periodicity with all polymers tested, which is yet to be assigned.

SAXS curves of samples containing the PDP amphiphile indicate the formation of similar hierarchical structures, which were already accounted for in the literature.¹ Nonetheless, the periodicity of all polymers with the PDP amphiphile remained largely similar (in the 199 kDa and 50 kDa polymers) or even increased (in the 63 kDa polymer, which changed morphology from cylindrical to lamellar, though) compared to the pure block copolymer, and compared to the copolymers with the Pd-SCS amphiphile, which caused severe

shrinking (Figure 2). Interestingly, the effect of the presence of the amphiphile on the periodicity of the hosting block copolymer has never been investigated before. In general, the specific binding of the amphiphile to the pyridine groups on the block copolymer should extend the P2VP chains (due to steric hindrance), and to space between them at the interfaces with the PS domains (Figure 3). The latter effect should cause increased folding of the PS chains to compensate for the lowered density at the interfaces. As a result, the P2VP/amphiphile domains should expand while the PS domains should shrink in size compared to the pure copolymer, and both effects could either compensate each other or result in an overall expansion of the lattice period (considering that a large volume was added to the polymer). Therefore, the strong decrease in the periodicity observed for samples containing the Pd-SCS amphiphiles was rather unexpected.

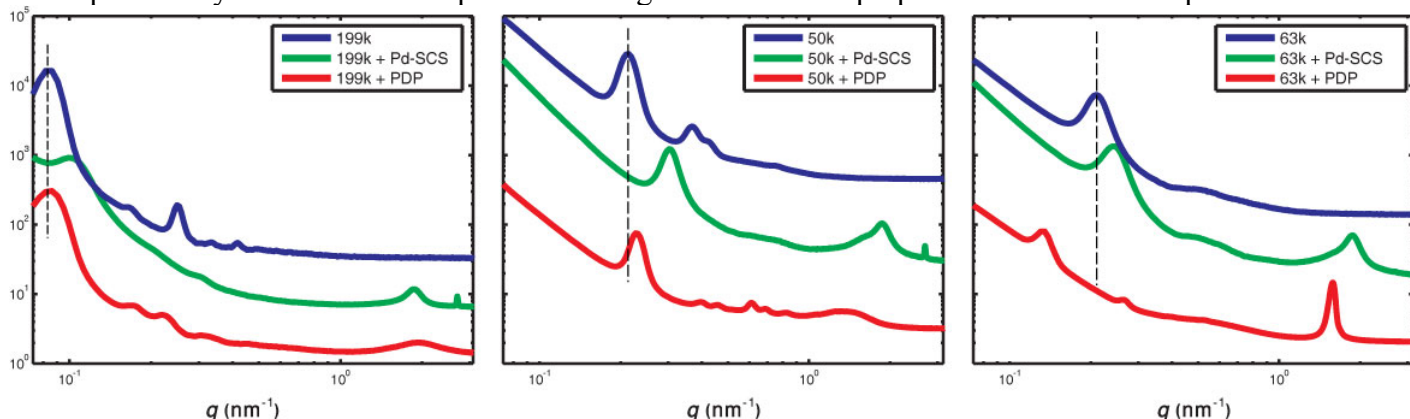


Figure 2. Amphiphile effect on the periodicity of the block copolymer in various block copolymers.

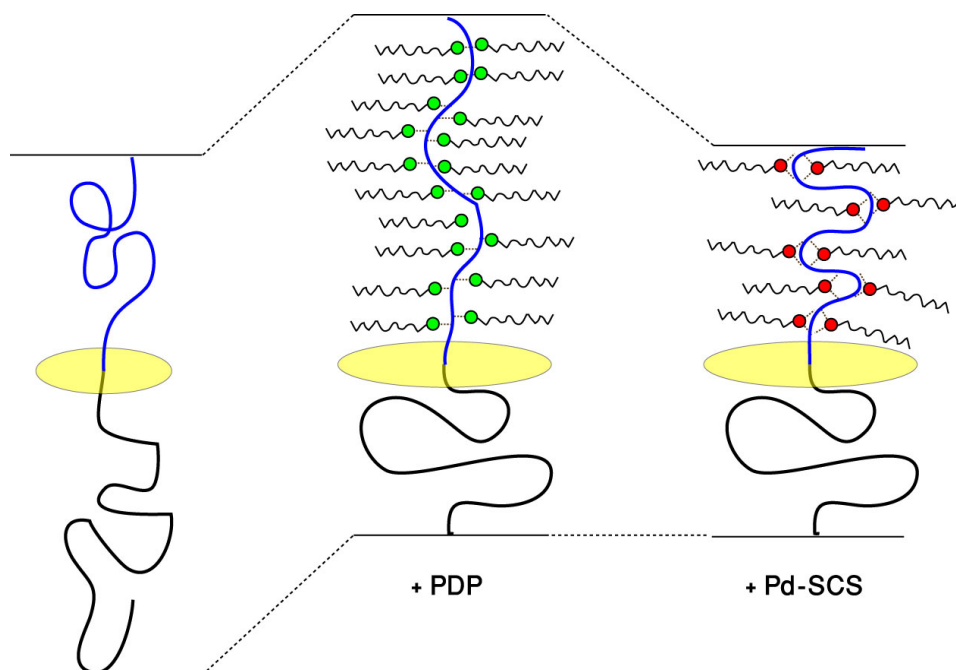


Figure 3. Cartoon illustrating the cross-linking effect of the Pd-SCS amphiphile and its influence on the overall block copolymer periodicity.

Following the results of the experiment at the ESRF, we have conducted various experiments to study the nature of bonding between the Pd-SCS amphiphile and the P2VP chains. X-ray photoelectron spectroscopy (XPS) information revealed an additional doublet for the Pd atoms after annealing of the composite film, indicating the covalent binding between the Pd atom and the nitrogen atom(s) of the pyridine groups. Additionally, quantitative dissolution experiments revealed that annealed samples containing Pd-SCS dissolved considerably more slowly compared to the pure copolymer or a copolymer containing the PDP amphiphiles. The only way to explain these data is to argue the Pd-SCS amphiphiles have a cross-linking effect on the P2VP blocks, which also induces extensive chain folding (i.e., by intramolecular cross-linking) that considerably reduces the average end-to-end distance of these chains and the overall periodicity of the copolymer (Figure 3). This option is possible considering that the sulfur ligands are rapidly interconverting at room temperature (as observed by nuclear magnetic resonance, NMR), which leaves the possibility for

pyridine groups to bind in their place (at least temporarily). Additionally, the presence of the amphiphiles with their long chains increases the effective cross section of each P2VP chains at the P2VP/PS interfaces, which causes the PS chains to extensively fold. In this situation, both polymer chains fold along the periodicity axis, which causes the considerable shrinking effect observed by SAXS. The cross-linking conjecture, claiming that the Pd-SCS actually binds *two* pyridine groups, can also explain the possible existence of excess of Pd-SCS amphiphile that led to the formation of pure domains of the Pd-SCS amphiphile indicated by the sharp peak at $q = 2.7 \text{ nm}^{-1}$.

Scattering curves of PDP-containing samples loaded with various metals mostly indicated the destruction of the hierarchical structure of the composites. The notable exceptions to these were samples loaded with AgNO_3 , which retained their hierarchical structures despite repeated loading and reduction cycles (Figure 4). Visual inspection also indicated that the samples turned gradually darker with repeated loading/reduction cycles, suggesting that selective incorporation of the Ag precursor into the hierarchical polymer matrix without destroying its fine structure was indeed obtained.

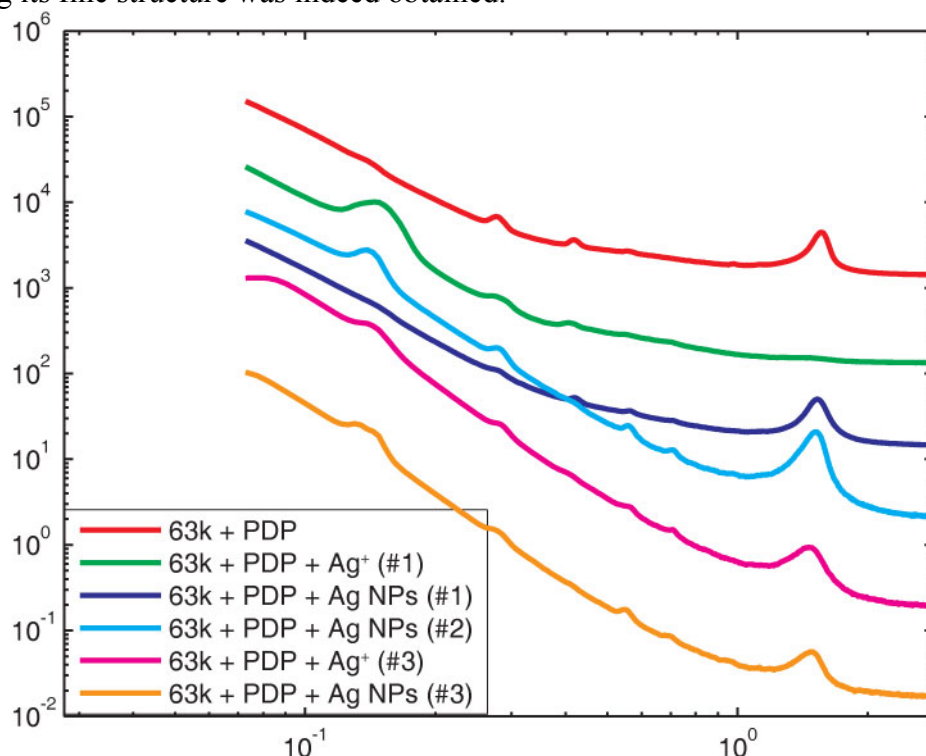


Figure 4. SAXS curves of PS-P2VP/PDP (0.8 equiv.) samples repeatedly loaded with AgNO_3 and reduced in NaBH_4 .

In summary, the experiment at ID02 provided valuable information on the hierarchical structure of block copolymer-organometallic amphiphile nanocomposites, which furthered our understanding of these composite materials and additionally opened new research directions (e.g., following the unexpected shrinking effect of the Pd-SCS amphiphiles on the copolymer). It should be emphasized that besides the high flux of photons, which facilitated the analysis of multiple samples within a relatively short time, the large q -range available at ID02 was crucial for obtaining clean data on samples featuring large block copolymer periodicities on the one hand and a fine hierarchical structure on the other.

References

- (1) Ruokolainen, J.; ten Brinke, G.; Ikkala, O. "Supramolecular polymeric materials with hierarchical structure-within-structure morphologies", *Adv. Mater.* **1999**, *11*, 777-780.