



<b>Experiment title:</b> Formation of Metal Nanoparticles in pH-responsive Polymeric Materials	<b>Experiment number:</b> SC-2482
<b>Beamline:</b> BM26B	<b>Date of experiment:</b> from: 21/06/2008 to: 24/06/2008
<b>Shifts:</b> 9	<b>Local contact(s):</b> Dr. Giuseppe Portale
<b>Date of report:</b> 27/02/2009  <i>Received at ESRF:</i>	

**Names and affiliations of applicants** (\* indicates experimentalists):

Professor SAIANI Alberto/ School of Materials, University of Manchester, Grosvenor str., Manchester M1 7HS, UK /+44 161 3065981/+44 161 3063586 / a.saiani@manchester.ac.uk  
 Professor ANASTASIADIS Spiros / Dept. Chemical Engineering, Aristotle University of Thessaloniki, 541 24, Greece / +30 2310 994245 / +30 2310 996269 / spiros@iesl.forth.gr  
 Professor VAMVAKAKI Maria / IESL, Found. for Res. & Techn.-Hellas, P.O. Box 1527, GR-71110 Heraklion, Greece /+30 2810 545019/+30 2810 391305/vamvakak@iesl.forth.gr  
 \* PAVLOPOULOU Eleni / IESL, Foundation for Res. & Techn. – Hellas, P.O. Box 1527, GR-71110 Heraklion, Greece / +30 2810 391311 / +30 2810 391305 / epavl@iesl.forth.gr  
 \* Dr. PORTALE Giuseppe / N.W.O., DUBBLE-CRG, ESRF, BP 220, Grenoble F38043, France / +33 (0)4 76 88 2536 / +33 (0)4 76 88 2412 / portale@esrf.fr

**Report:**

The impregnation of Pt nanoparticles within two different polymeric matrices was investigated in this experiment. The nanoparticles size and number distribution, as well as their spatial location within the organic nanostructures, have been studied with respect to the polymer-to-metal loading ratio, which was utilized as a control parameter for tailoring the nanoparticles properties, while the effectiveness of the synthetic route on the synthesis of stable polymer-metal nanohybrids have been explored by applying two methods for the preparation of the nanoparticles.

The two types of polymeric matrices that have been used in our research for the growth of colloidal Pt nanoparticles were: (1) Polymeric micelles formed by the pH-driven self-assembly of amphiphilic diblock copolymers, poly(hexa(ethylene glycol) methacrylate)-*b*-poly(2-(diethylamino)ethyl methacrylate), PHEGMA-*b*-PDEA. At low pH the copolymer is in its “unimer” state, while an increase of the pH results in the formation of micelles. (2) pH-sensitive PDEA-microgels which exhibit reversible swelling properties in water by adjusting the solution pH. At low pH the microgel particles are swollen, while an increase of the pH leads to hydrophobic latex particles. Metal nanoparticles were synthesized within both the micellar cores of the diblock copolymers and the microgels by the incorporation of the metal precursor due to electrostatic interactions, i.e., by the addition of H<sub>2</sub>PtCl<sub>6</sub> and the subsequent metal reduction, or by the metal incorporation due to polymer-metal coordination, using K<sub>2</sub>PtCl<sub>6</sub> instead of H<sub>2</sub>PtCl<sub>6</sub> at high pH. Three series of polymeric nanostructures impregnated with Pt nanoparticles, were studied; PHEGMA-PDEA polymeric micelles and PDEA microgels loaded at five different polymer-to-metal ratios at a) low and b) high pH, using H<sub>2</sub>PtCl<sub>6</sub> as the metal precursor, and c) micelles and microgels loaded at high pH with the K<sub>2</sub>PtCl<sub>6</sub> salt. The first two series were designed in order to study the size, number density and the location of the nanoparticles within the matrices, while the third allowed us to investigate the polymer-metal interactions. Dilute aqueous solutions of these systems were characterised using Small Angle X-ray Scattering (SAXS) and thus the form factor of the polymer-metal nanohybrids was obtained.

SAXS data were recorded on a two-dimensional position sensitive detector. Two different energies of the X-ray beam were used, 15keV and 8keV, each one for a different sample-to-detector distance, 2 m and 7 m respectively, and thus a wide scattering vector range was covered,  $0.045 < q < 6.4 \text{ nm}^{-1}$ . The two-dimensional images were radially averaged around the center of the primary beam, in order to obtain the isotropic SAXS intensity profiles. The scattering patterns from a specimen of wet collagen (rat tail tendon) and Silver Behenate were used for calibration of the  $q$  scale of the scattering profiles. Lupolen and Eltex were used as reference samples for the intensity calibration in absolute units ( $\text{cm}^{-1}$ ). The data have been normalized to the intensity of the incident beam (in order to correct for primary beam intensity decay) and corrected for absorption and background scattering. Two ionization chambers placed before and after the sample, were utilized for the measurement of the incident and the transmitted beam. The background correction was made by subtracting from the total intensity the contribution of density fluctuations evaluated from measuring pure water. All samples were placed inside glass capillary tubes of 2 mm diameter and the measurements were conducted at room temperature.

The systems under study were characterised during the three steps of the metal nanoparticle synthesis; the original polymer dispersions in water, the metal – loaded polymer matrices and the metal nanoparticle-containing polymers after reduction. Two sets of data showing comparatively the scattering profiles for the three synthetic steps are shown in Figures 1a and 1b, for a solution of micelles and microgels respectively. The complexity of the final system necessitates the characterization of all three steps, since each one can provide information for a different phase.

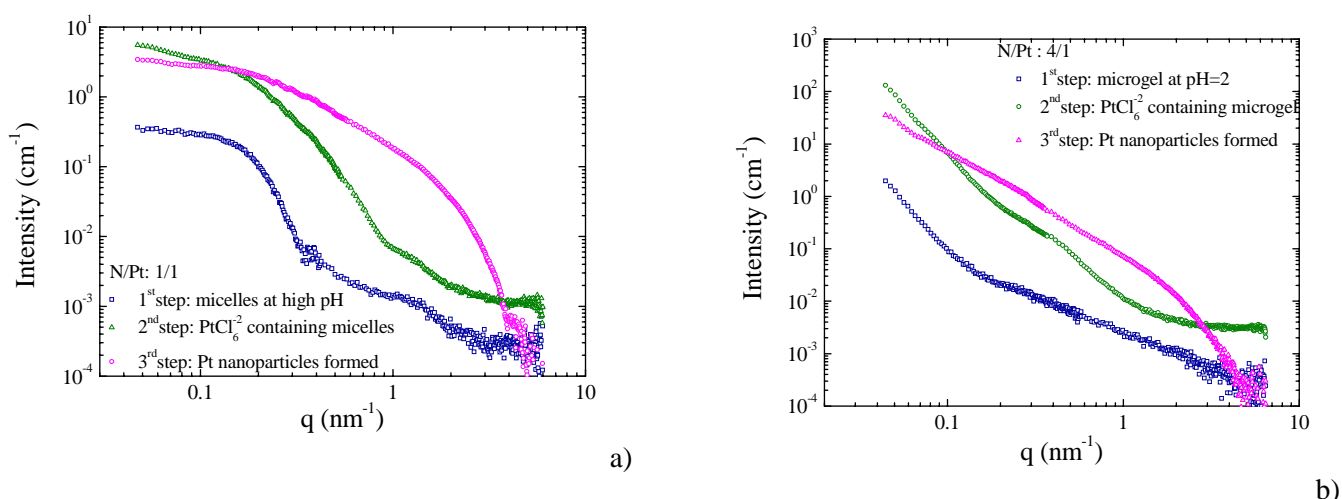


Figure 1: The SAXS intensity profiles for the various synthetic steps followed for the formation of Pt nanoparticles within the PHEGMA-PDEA micelles (a) and within the PDEA microgels (b).  $\text{K}_2\text{PtCl}_6$  has been used as the metal precursor in both cases, while the polymer-to-metal ratio was 1/1 for the micelles and 4/1 for the microgels.

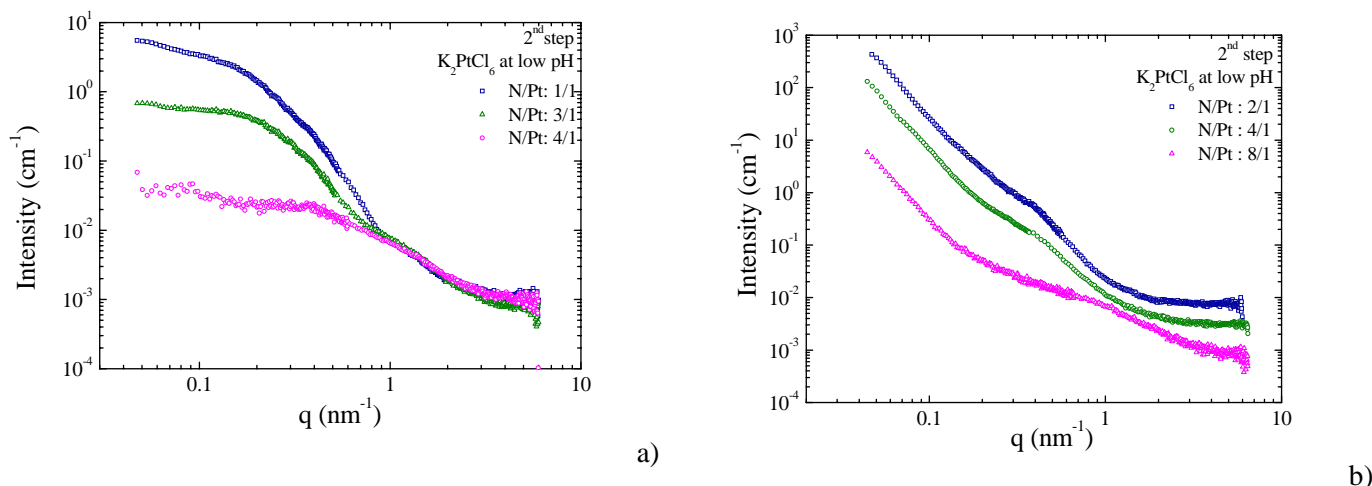


Figure 2: The SAXS intensity profiles for the metal incorporation in PHEGMA-PDEA micelles (a) and PDEA microgels (b), using  $\text{K}_2\text{PtCl}_6$  at low pH, for the various polymer-to-metal ratios.

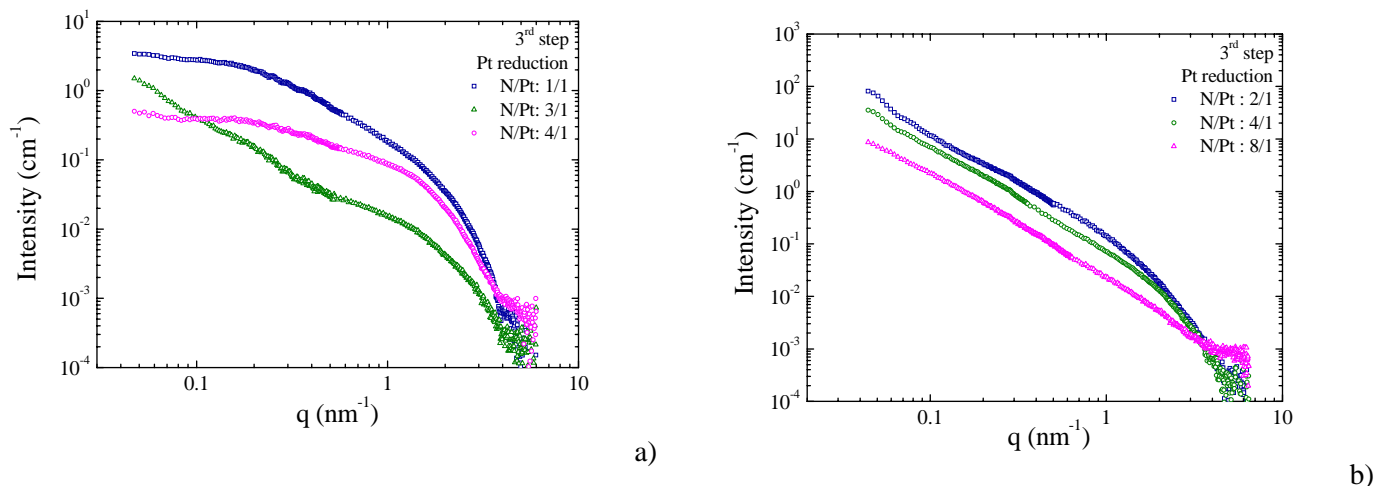


Figure 3: The SAXS intensity profiles of the Pt nanoparticle-containing PHEGMA-PDEA micelles (a) and PDEA microgels (b) that were obtained after the reduction of the solutions presented in Figures 2, for the various polymer-to-metal ratios.

The scattering profile of the pure micellar solution (Fig. 1a) corresponds to the form factor of a core-shell structure, with core radius 14.2nm and a homogeneous shell with a thickness of 1.55nm. The core polydispersity is estimated as well. After the incorporation of the metal precursor, the scattering profile still corresponds to that of a core-shell structure, but the scattered intensity is increased by an order of magnitude, due to the enhancement of the electron density difference by the dispersion of the metal in the micellar core. The increase of the polymer-to-metal ratio affects the electron density of the core and thus the contribution of the core to the total scattered intensity decreases, resulting in the profiles presented in Figure 2a. Moreover, the form factor analysis revealed a decrease in the core radius, while the shell thickness remains unaffected. Figure 3a shows the scattering profiles acquired for the reduced samples. For all the three different polymer-to-metal ratios, the contribution of the nanoparticles scattering is very much pronounced in the high  $q$  range and a constant particles size of around 2nm diameter is estimated.

As far as the pure microgel solutions are concerned, two contributions are apparent in their scattering profiles, one arising from the spherical shape of the microgel and one arising from the microgels network. At low pH the microgel particles are swollen, their radius ( $\sim 150$ nm, according to static light scattering measurements) exceeds the sizes detected in the  $q$  range accessed and, thus, only the Porod scattering is obvious below  $0.1\text{nm}^{-1}$  (Fig.1b). Above this value, a  $q^{-1.3}$  dependence is observed and is attributed to the scattering from the loose network in the swollen state. The Porod scattering is still obvious after the metal incorporation and is followed by a bump. This bump is observed for all the polymer-to-metal ratios under study (Fig. 2b) and it was attributed to condensation of the metal complexes within the microgel particles. As expected, the total scattering intensity increases as the metal loading of the solutions increases. After the reduction of the metal complex, Pt nanoparticles are formed and their size is estimated from the profiles shown in Figure 3b to be around 1.5nm in diameter, very close to the values obtained for the nanoparticles formed within the micellar matrices.

Besides the data presented herein, very interesting results also came up regarding the influence of the chemical route applied to the nanoparticles properties and the nanohybrids characteristics, for both the polymeric matrices. The amount of data obtained during this experiment and the quality of the information revealed from the data analysis ensure the publication of two scientific articles, one for each polymeric matrix studied.