

The Formation of Metal Nanoparticles in pH-responsive Block Copolymers and Hydrogels

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Introduction

The self-assembly of amphiphilic block copolymers in aqueous environment has attracted great scientific interest [1]. The use of water as a solvent is advantageous in view of a number of potential applications, like drug delivery, biomolecule separation, catalysis, etc. The formation of micelles following a simple change of the solution conditions (e.g., pH, temperature, etc.) became possible with the synthesis of double hydrophilic diblock copolymers which can respond to changes in their environment [2]. The formation of micelles with varying pH is particularly advantageous when a completely hydrophobic core is needed. The cores of such micelles can be utilized as nanoreactors for the synthesis of metal nanoparticles [3], whose properties are controlled by their size, shape and structure. These nanoparticle hybrids possess distinct advantages regarding their magnetic, optoelectronic and catalytic properties. At the same time, pH-responsive hydrogels based on either acidic or basic monomer units are particularly attractive for use in biomedical and biotechnological applications such as protein absorption, drug delivery and immobilization of biomolecules and as hosts for the growth of inorganic nanoparticles [4].

Experimental

In the present work we have employed two types of polymeric matrices for the growth of colloidal metal particles. In the first case, the micellar cores of double hydrophilic block copolymers were utilized as the nanoreactors whereas in the second case pH-sensitive microgels were used. PHEGMA-*b*-PDEAEMA diblock copolymers were synthesized by group transfer polymerization chemistry in THF. The solution behavior of the copolymers as a function of the degree of ionization of the DEAEMA block was investigated by dynamic light scattering (DLS), ¹H NMR, and AFM. pH-sensitive microgels with a diameter of ~250nm were synthesized by emulsion copolymerization of DEAEMA with a bifunctional cross-linker at pH 9. Their reversible swelling properties in water by adjusting the solution pH were studied by DLS. Metal nanoparticles were synthesized within both the micellar cores and the microgels by the addition of H₂PtCl₆ and subsequent reduction using NaBH₄. The nanoparticles were investigated by TEM and XRD.

Results and discussion

Figure 1 shows the hydrodynamic radii data following the analysis of the autocorrelation functions obtained by DLS for a 0.1 wt% solution of PHEGMA₅₀-*b*-PDEAEMA₅₀ as a function of the degree of ionization of the DEAEMA monomers, α [5]. For high α (low pH), the total scattering intensity is very low whereas two processes are observed in the distribution of relaxation times: one corresponding to the translational diffusion of single chains with size ~3.5nm (Figure 1) and one due to aggregates (~60 nm) with low intensity (thus, very few). Only when the degree of ionization becomes less than 0.2 (fewer than 20% protonated monomers), the total scattering intensity increases significantly and the two processes now correspond to micelles of size ~11 nm and of micellar aggregates (again a few) with size ~80 nm. Further decrease of α leads to an increase of the micelle size to that (~15nm) observed at very high pH

10 [6]. The ¹H NMR spectra (not shown) for solutions of PHEGMA₅₀-*b*-PDEAEMA₅₀ as a function of α show a continuous shift of the DEAEMA NMR-peaks at δ 1.4, 3.4, 3.65 and 4.45 ppm towards high fields due to the deprotonation of the DEAEMA units whereas the formation of micelles leads to the disappearing of the DEAEMA peaks because this block forms the micellar core.

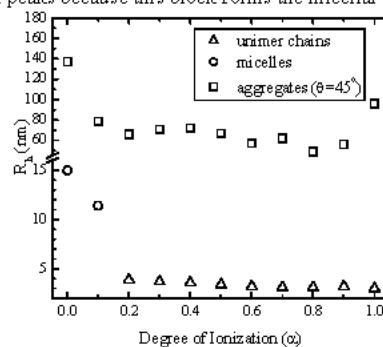


Figure 1. Hydrodynamic radii of unimers, micelles and aggregates obtained by DLS for a 0.1 wt% water solution of PHEGMA₅₀-*b*-PDEAEMA₅₀ at various α .

Figure 2 shows the XRD spectra of PHEGMA₅₀-*b*-PDEAEMA₅₀ after the metal reduction for N:Pt 3:1 and 1:1. The peaks identified characterize the crystal structure of Pt verifying the formation of metal nanocrystals within the micellar core. The width of the peaks correspond to nanocrystals of 3-3.5nm. Note that analysis of TEM images results in average nanoparticle dimensions of 1-2 nm. Evidently the smaller nanoparticles observed by TEM are amorphous.

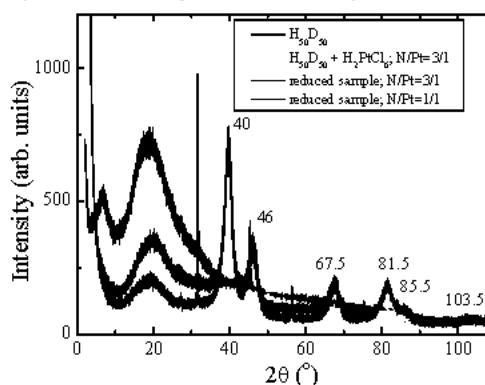


Figure 4. X-ray diffractograms of metal nanoparticles within the micelle cores of PHEGMA₅₀-*b*-PDEAEMA₅₀ for N:Pt 3:1, 1:1

Conclusions

The micelle formation in aqueous solutions of double hydrophilic PHEGMA-*b*-PDEAEMA diblock copolymers and the influence of the solution pH and the corresponding ionization of DEAEMA was investigated. Besides, the formation of metal nanocrystals was studied within the micelle core for various degrees of polymer-to-metal loadings. Similarly, metal nanocrystals can be formed within pH-sensitive microgels (~250nm in diameter), synthesized by emulsion copolymerization of DEAEMA, which also exhibit reversible swelling properties in water by adjusting the pH [7]

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