

TEMPLATING OF GOLD NANOPARTICLES USING POLY(ETHYLENE OXIDE)-*block*-POLY(1H,1H- DIHYDROPERFLUOROOCXYL METHACRYLATE) MICELLAR FILMS

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ABSTRACT

Well-defined diblock copolymers consisting of a hydrophilic poly(ethylene oxide) (PEO) and CO₂-philic poly(1H,1H-dihydroperfluorooctyl methacrylate) (PFOMA) block were utilized to the self-assembly of gold nanoparticles. Spin-coated thin films of poly(FOMA_{20k}-*b*-EO_{20k}) with gold salts from chloroform formed spherical micelles with a PFOMA core and PEO corona. The films were induced to undergo a transition by annealing in supercritical CO₂; consequently, the PEO segments formed the core with a PFOMA corona. The gold salts which were initially dispersed within the corona (the PEO phase) of the micelles followed the morphological inversion and became a single gold particle within the core. The gold nanoparticles which had average diameter of 20 nm were well ordered in the reorganized micellar film.

INTRODUCTION

Templating self-assembly of nanoparticles into specific structures can provide controlled fabrication of nanometer-sized building blocks with unique electronic properties [1]. The ability to control the chemical composition and structure of block copolymers allows these materials to be ideal templates for control over the size, particle density, and spatial location of inorganic nanoparticles. Hybrid systems constituting self-assembled amphiphilic block copolymers and metal/semiconductor nanoparticles are important in modern material science and are extensively investigated [2-5]. Such design flexibility has been exploited in the efficient fabrication of novel functional materials such as nanostructured solar cells, photonic devices, highly efficient catalysts, and high density magnetic storage media. However, despite the importance of controlling the arrangement of nanoparticles within the periodic structure of the block copolymer, an establishing such control has been difficult [6-9]. The particular interest is controlling the assembly of nanoparticles at the interface between different polymer domains. Recently, there has been a growing interest to control the nanoparticle location within block copolymer domains [10-12].

In this work, we utilize poly(FOMA_{20k}-*b*-EO_{20k}) diblock copolymers to form micelles, i.e. small compartments in which the gold particles are generated and which allow us to prepare thin, coherent films with a well controlled particulate structure. We also demonstrate that it is possible to obtain a nanostructured block copolymer nanocomposite thin film with a switchable spatial distribution of embedded nanoparticles between the core and the corona.

EXPERIMENTAL

The block copolymer studied in this work is poly(1H,1H-dihydroperfluorooctyl methacrylate)-*block*-polyethylene oxide (poly(FOMA-*b*-EO)), with a $Mn_{\text{PFOMA}}/Mn_{\text{PEO}} = 20000/20000$, as determined by ¹H NMR. The block copolymer was synthesized by atom transfer radical polymerization (ATRP) of FOMA using MPEO-Br as macroinitiator in the mixed solvent of trifluorotoluene and benzene, as described previously [13]. The molecular structure of poly(FOMA-*b*-EO) is depicted in Fig. 1. The block copolymer was dissolved in chloroform at 0.5 % w/w. Additional solutions containing gold precursor were prepared. Films were prepared by spin-coating of polymeric micellar solutions onto mica. Supercritical CO₂ annealing was performed by loading the samples into a fixed reactor, which is subsequently sealed and pressurized with carbon dioxide (99.99%) using high pressure syringe pump (ISCO-Model 260D) and heated to the desired temperature in a water bath. It was observed that both of the blocks were in a plasticized state under the experiment conditions; 70 °C and a pressure of 2000 psi. After a period of 24 h, the reactor was cooled to room temperature and depressurized by venting CO₂ as a vapor from the top of the reactor. The film was floated on water and off the mica substrate and deposited onto a copper grid coated with carbon. Water was allowed to evaporate from the grid at atmospheric pressure and room temperature.

The morphologies of the thin films were investigated before and after annealing by transmission electron microscope (TEM) using a Hitachi H-7500 instrument operated at 80 kV.

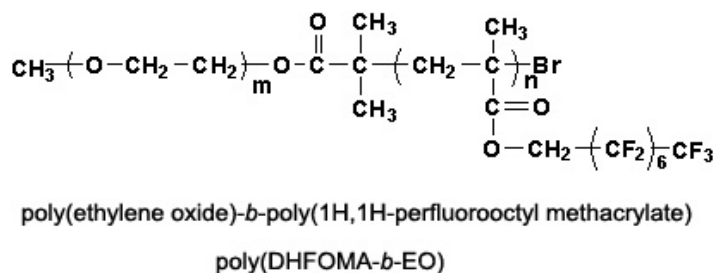


Fig. 1. The chemical structure of poly(DHFOMA-*b*-EO)

RESULTS AND DISCUSSION

The strategy for assembly of diblock copolymers and nanoparticles relies on tailoring the surface chemistry of nanocrystal such that it exhibits a stronger affinity for one block [14]. In this study, we

compatibilized gold nanoparticles, thereby rendering the nanocrystal-PEO system to interact favorably with PEO domains. The process is schematically shown in Figure 2. In the first step, poly(FOMA_{20k}-*b*-EO_{20k}) block copolymer has been employed as a micelle forming block copolymer. Gold was used as the small particles to be generated inside coronas. Under the experimental conditions poly(FOMA-*b*-EO) associates to form micelles in chloroform. When LiAuCl₄⁻ was added to such a solution, the salt was slowly solubilized as Li⁺ ions formed a complex with polyethylene oxide units of the block copolymer as shown in the second stage of Figure 2. The tetrachloroaurate ions are thus bound as counter ions within the PEO block of the micelles. Complex formation of the polyethylene oxide block with LiAuCl₄⁻ enhances considerably the stability of the micelles [4]. The last two steps comprise film formation and conversion of the inorganic precursor to a nanoparticle within the micellar compartment.

Figure 3a shows TEM image of a monolayer of micelles of poly(FOMA_{20k}-*b*-EO_{20k}) block copolymer. PFOMA cores of about 26 nm in diameter are embedded in a continuous PEO (corona) matrix. The continuous phase is marked by the dark dots, which is resulted from the reduction of LiAuCl₄ upon interaction with the electron beam and leads to the formation of gold particles in sizes smaller than 1 nm in diameter. The nanoparticles are indeed preferentially located within the continuous PEO phase.

TEM image of the same sample annealed at 70 °C and a pressure of 2000 psi in CO₂ is presented in Figure 3(b). Upon annealing the diblock in scCO₂ which is highly selective toward the fluorinated block, the structure is inverted and the PEO chains constitute the core of the micelle.

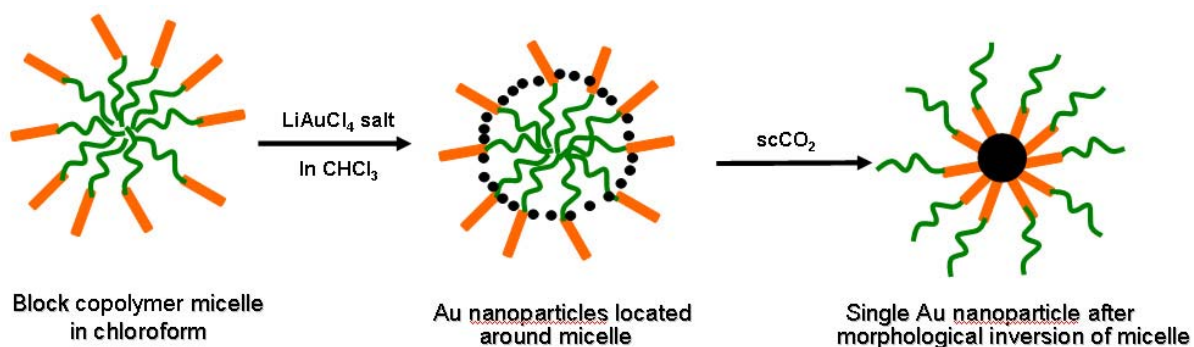


Fig. 2 Scheme of the formation of nanoparticles in a block copolymer micelle; i) Micelle formation in chloroform; ii) Loading with the precursor component; iii) Transformation to a single gold particle.

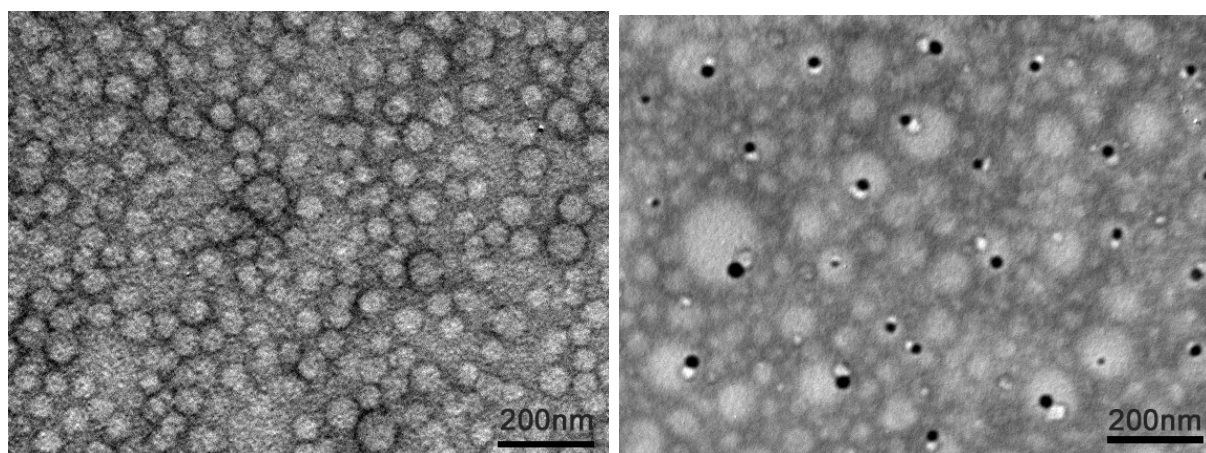


Fig. 3 TEM images showing the formation of gold nanoparticles in PEO blocks.
(A: room temperature, B: annealing at 70 °C and 2000 psi in CO₂ for 24h)

The film indicates that the structure of the aggregates has been completely inverted in scCO₂ environment to form PEO cores surrounded by PFOMA shell. This phase transformation opens up the possibility of controlling micelle formation and morphology by adjusting the solvent quality through manipulation of pressure and temperature of the system. Indeed, detailed studies on this system demonstrate that it is also possible to tune micellar size through careful adjustments of CO₂ density [15]. From Figure 3b it is evident that the inversion to the initial morphology has been achieved, and the nanocrystals are constrained to follow the morphological change; i.e., they were transformed into a single particle in the morphology of the dispersed PEO phase. The PEO core domain has an average characteristic size of 100 nm with a broad size distribution ranging from 40 to 160 nm and contain only one nanoparticle with average characteristic size of 20 nm per micelle.

CONCLUSIONS

Self-assembly of poly(FOMA_{20k}-*b*-EO_{20k}) block copolymers with gold salts formed gold particles of sizes about 1 nm dispersed in PEO coronas through the spin coating of chloroform solution. Annealing the film in scCO₂, which is highly selective toward the fluorinated block, leads to the inversion of the morphological structure and PEO chains constituted the core of the micelles. The film indicates that the structure of aggregates has been completely inverted in scCO₂ environment to form PEO cores surrounded by PFOMA shell. The PEO core domains have an average size of 100 nm and contain only one nanoparticles with average characteristic size of 20 nm per micelle. Our findings demonstrate the feasibility of using selective solvent annealing as a means of controlling composite nanostructure in a dynamic fashion. Thus phase inversions enabling the control of the nanocomposite structure can be accomplished by exposing a block copolymer to any selective solvent. The use of supercritical fluids offers the possibility of tuning the morphology of the polymer in a very controlled manner.

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