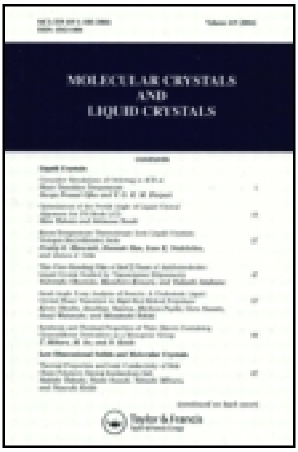

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# Semi-fluorinated Block Copolymer Directed Ordering of Gold Nanoparticles in Thin Films *via* Solvent Vapor Annealing

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*The block copolymer thin films were prepared by spin casting micellar solutions of poly(ethylene oxide)-b-poly(1H,1H dihydroperflurooctyl methacrylate)(PEO*$_{5k}$*-b-PFOMA*$_{22k}$*) in chloroform with or without gold salts. Upon fluorinated solvent vapor annealing, the disordered morphology of as-casted PEO*$_{5k}$*-b-PFOMA*$_{22k}$ *thin films was changed to the phase inverted ordered morphology of spherical PEO cores in PFOMA continuous phase. The phase inversion strategy of the solvent annealing was found to enhance the long-range positional ordering of the thin films. The results suggest that an organized pattern of gold nanoparticles could be afforded inside the PEO domains of the hybrid thin films.*

**Keywords** Nanoparticles; self-assembly; semifluorinated diblock copolymer; solvent vapor annealing; thin film

## Introduction

Over the past few decades, many strategies have been devised to synthesize metallic nanoparticles using block copolymers (BCPs) to afford nanomaterials with unique optical, magnetic, electronic, and catalytic properties [1,2]. In particular, gold nanoparticles (Au-NPs) have attracted great attention for applications as catalysts, chemical sensing and electronic devices [3,4]. The fabrication of thin layers is critical to control site specific orientation of particles at nanoscale level. To control the size and shape of the metallic nanoparticles in BCPs, the *ex situ* phase transition synthetic approach is widely used [5]. In contrast, the facile *in situ* protocol can be used for selective preparation of nanoparticles in BCPs [6]. Applying external fields, the orientation of nanodomains can be restructured

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in BCPs thin films [7,8]. Recently, solvent vapor annealing is considered as a powerful strategy to fabricate ordered morphology [9].

Semifluorinated BCPs are amphiphilic, which have self-assembly characteristics of BCPs and the unique properties of fluorinated polymers [10]. Although, a variety of methods have been developed for selective incorporation of naoparticles in desired blocks, only a few results have been reported for the ordering of Au-NPs with semifluorinated BCPs thin films [5,6].

Herein, an *in situ* approach for preparing ordered Au/BCP hybrid materials has been reported by employing a facile solvent vapor annealing of Au-loaded PEO-*b*-PFOMA thin films. Gold precursor $LiAuCl_4$ formed complex with PEO blocks, which was reduced into Au-NPs. Upon PF-5080 solvent annealing, the PEO domains were ordered in the PFOMA continuous phase with a Au-NP in each domain.

## Experimental

### Synthesis of Block Copolymers by ATRP

The semifluorinated diblock copolymers poly(ethylene oxide)-*b*-poly(1H,1H-dihydroperfluorooctyl methacrylate) (PEO-*b*-PFOMA) were synthesized by atom transfer radical polymerization (ATRP) of FOMA using PEO-Br as the macroinitiator as reported previously [11]. In this study, commercially available $PEO_{5k}$ was used to prepare $PEO_{5k}$-*b*-$PFOMA_{22k}$. The chemical structure of PEO-*b*-PFOMA is shown in Fig. 1.

### In-situ Synthesis of Gold Nanoparticles Using BCPs

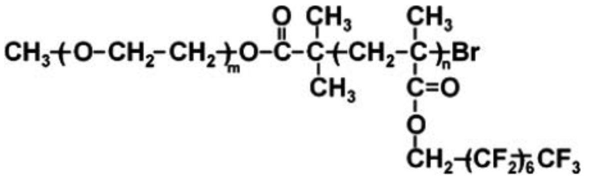
$PEO_{5k}$-*b*-$PFOMA_{22k}$ was dissolved in chloroform to yield 0.5 wt% solution. $LiAuCl_4$ loaded micellar solution was prepared by adding 0.1 wt% of $LiAuCl_4$ into the solution.

### Thin Film Preparation

Two kinds of thin films were prepared on substrates by spin-coating of the BCP micellar solution and $LiAuCl_4$ treated micellar solution. The prepared films were dried in the ambient condition for 15 min.

### Ordering of the Micellar Thin Film

For morphology study, the thin film coated on a TEM grid was placed in a glass vessel of the reservoir of PF-5080 (perfluroalkanes). The temperature of the fluorinated solvent



$CH_3\text{-}(O\text{-}CH_2\text{-}CH_2)_m\text{-}O\text{-}C(=O)\text{-}C(CH_3)_2\text{-}(CH_2\text{-}C(CH_3)(C(=O)\text{-}O\text{-}CH_2\text{-}(CF_2)_6CF_3))_n\text{-}Br$

**Figure 1.** Structure of the PEO-*b*-PFOMA BCP.

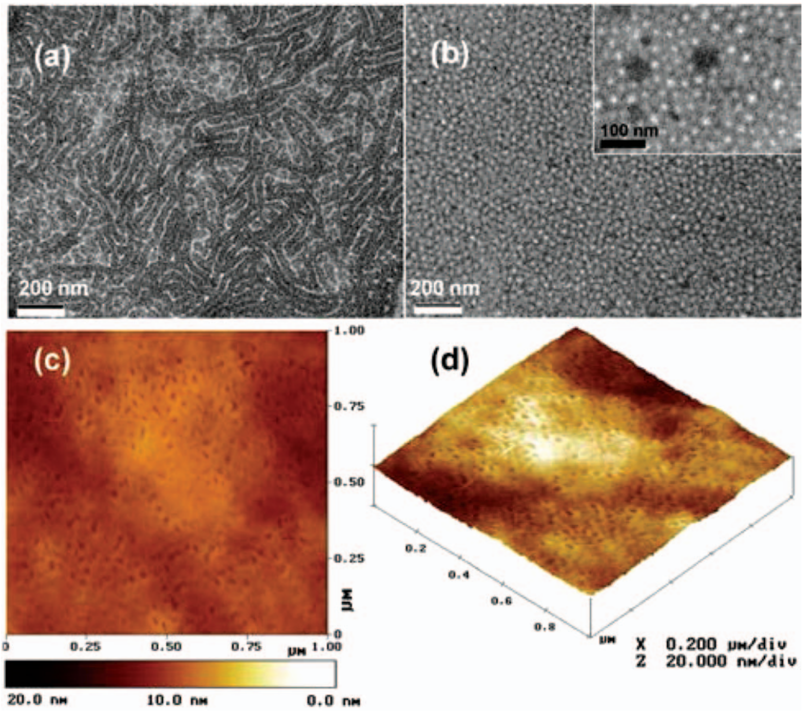


**Figure 2.** TEM images of PEO-*b*-PFOMA diblock copolymer (a) as-cast thin film; (b) thin film after PF-5080 solvent vapor treatment for 3 h, and (c, d) the corresponding height and 3-D image of 2b, respectively.

vapor was always kept at 70°C. The PF-5080 vapor induced the chain mobility of the BCP and developed ordered nanostructures.

## Measurements

$^1$H-NMR spectra of PEO-*b*-PFOMA BCPs were recorded in a mixed solvent of $CFCl_3$ and $CDCl_3$ using a JNM-ECP 400 (JEOL) spectrophotometer. The morphology of the thin films was investigated by transmission electron microscope (TEM) using a Hitachi H-7500 instrument operated at 80 kV. The tapping-mode atomic force microscopy (TM-AFM) measurements were carried out in a Digital Instruments multimode (Veeco) at room temperature. The UV-visible spectra were measured using a Perkin Elmer UV-visible spectrophotometer (Lambda 40).

## Results and Discussion

It was reported that semifluorinated BCPs with different block lengths gave various film morphologies [15,16]. $PEO_{5k}$-*b*-$PFOMA_{22k}$ was used for solvent annealing with or without AuNPs loading. The thin films were annealed under saturated PF-5080 vapor at 70°C. This temperature was chosen to keep the BCP above the glass transition temperature ($T_g$) of PEO and PFOMA [12]. Spin-casted thin films were reorganized into thermodynamically stable morphologies upon annealing [7,8]. It is speculated that the fluorinated solvent vapor

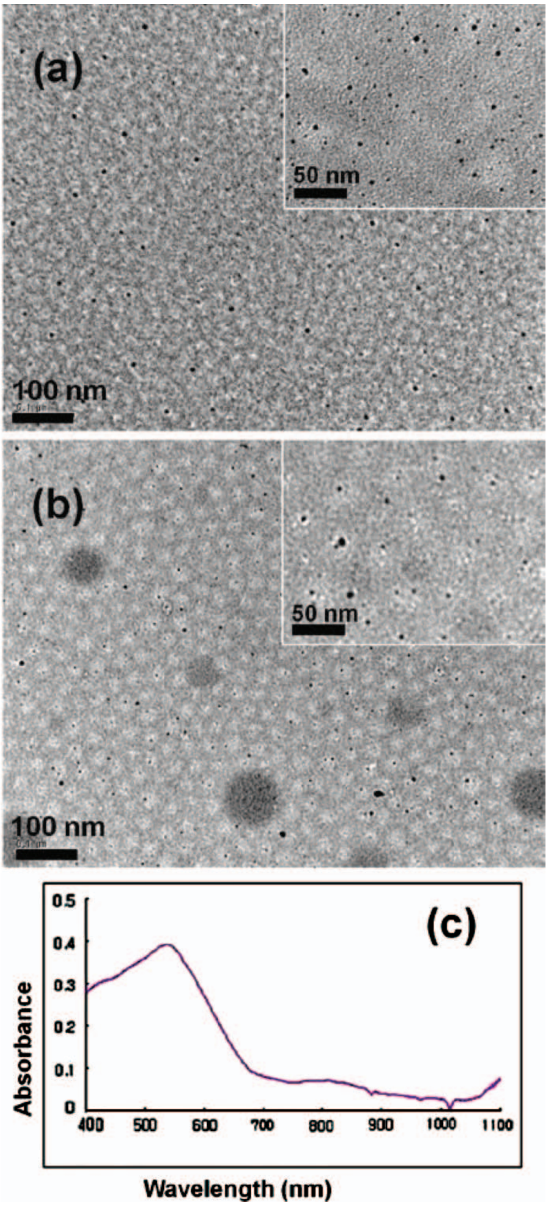


**Figure 3.** TEM images of Au-NPs produced in thin films of PEO-*b*-PFOMA, (a) as-cast film from chloroform solutions and (b) after PF-5080 solvent vapor treatment for 3 h, and (c) UV-vis absorption spectra of Au-NPs.

effect on the PEO-*b*-PFOMA thin film would be markedly different from that of thermal [7,8] or conventional solvent vapor annealing [9].

The TEM image of as-cast $PEO_{5k}$-*b*-$PFOMA_{22k}$ thin films from chloroform (a good solvent for PEO chains) is shown in Fig. 2a. The darker phase corresponds to the high electron density component of PFOMA blocks and the brighter phase represents PEO blocks. It can be seen that the as-cast film has combined aggregates of cylindrical and vesicular. A dramatic morphological transition has been observed in the thin films upon PF-5080 solvent treatment for 3 h (Fig. 2b). PEO domains can clearly be distinguished as bright sphere. The area of the film shows PEO nanodomains (diameter 24 nm) in the PFOMA continuous phase. Longer annealing times (4 h to 18 h) also gave a similar ordered morphology with PEO domains in PFOMA continuous phase, indicating 3 h treatment is enough to reach a thermodynamically equilibrium state.

The height and 3-D TM-AFM images (Fig. 2c–d) are consistent with the corresponding TEM image of Fig. 2b. The bright domains correspond to soft materials which induce more phase lag of the cantilever, while the dark domains correspond to the hard materials which induce less phase lag [13]. Since the crystalline PEO segments are harder than the amorphous PFOMA segments, the darker domains can be attributed to PEO and the brighter one is for PFOMA segments.

Well-ordered Au-NPs impregnated nanodomains were attempted by the solvent annealing approach. $LiAuCl_4$ loaded micellar solutions were prepared by adding 0.1 wt% of $LiAuCl_4$ into the block copolymer micellar solutions. When the solution was treated with solid $LiAuCl_4$, the salt was slowly solubilized as the $Li^+$ ions complexes with PEO units of the BCPs and the tetrachloroaurate ions are bound as counter ions within the PEO phase of the micelles [14]. Figure 3a shows TEM image of the thin films which was prepared from the $LiAuCl_4$-loaded micellar solution. The bright colored PEO phase is occupied by Au-NPs (dark dots) resulting from the reduction of gold ions in the presence of PEO [15]. As shown in Fig. 3a, Au-NPs are well dispersed in the PEO phase but were not observed in the PFOMA phase. In the thin films, the average diameter of the Au-NPs was *ca.* 6 nm.

The Au-loaded thin film was annealed in PF-5080 vapor at 70°C for 3h. In the TEM image of the annealed film (Fig. 3b), it is observed that the morphology was reorganized comprising bright isolated PEO cores and gray continuous PFOMA phase. They have absolutely inversed contrast compared to the as-cast image as shown in Fig. 3a. In the inversion process, the Au-NPs were constrained to follow the morphological change and they resided in the PEO domains. This result reveals that Au-NPs were selectively located in the PEO phase and effectively moved along with the PEO chains during the phase-change upon solvent annealing. Several large beadlike aggregates are seen discretely in the image (Fig. 3B), which may be attributed to heterogeneity of the block copolymer composition. The beadlike deformation was also persistent after annealing without gold precursor as shown in the inset of Fig. 2B.

The formation of elemental gold was also confirmed by UV-visible absorption spectroscopic analysis. Figure 3c demonstrates the UV-visible absorption spectra of Au-NPs. The absorption appears at 540 nm, which is conventional plasmon band for spherical gold nanoparticles. The extinction coefficient values of the particles are consistent with the reported results [14,16].

## Conclusions

In conclusion, this study demonstrated site specific fixation of Au-NPs within PEO domains of the self-assembled $PEO_{5k}$-*b*-$PFOMA_{22k}$ thin films *via* fluorinated solvent annealing. The PF-5080 solvent annealing of Au-loaded $PEO_{5k}$-*b*-$PFOMA_{22k}$ copolymers resulted in well dispersed Au-NPs in the PEO cores with PFOMA continuous phase. The solvent vapor treatment is considered to be an efficient way for ordering the morphology of the $PEO_{5k}$-*b*-$PFOMA_{22k}$, and this strategy may be useful for fabrication of well ordered hybrid thin films for versatile applications.

## Acknowledgments

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