

GOLD/SEMI-FLUORINATED BLOCK COPOLYMER NANOCOMPOSITES DEVELOPED IN THIN FILM WITH ANNEALING

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Herein, an approach for preparing the ordered structures of Au/polymer nanocomposites is discussed, which employs solvent vapor, supercritical CO₂ and thermal annealing process for Au-loaded poly(3-hexyl thiophene)-block-poly(1H,1H-perfluorooctyl methacrylate) (P3HT-b-PFOMA) thin films. The block copolymers underwent microphase separation and self-assembly into well-defined and organized nanofibrillar-like morphology from their micelle solution. The gold nanoparticles were stabilized by the interaction of the sulfur atoms of P3HTs with the gold surface and they dispersed in the P3HT phase. The length of nanofibrils increased a little with pronounced branching after thermal annealing, solvent annealing and scCO₂ annealing in the micellar films with the Au nanoparticles.

Keywords: *1H, 1H-perfluorooctyl methacrylate, poly(3-hexylthiophene), block copolymer, gold nanoparticles, annealing.*

1 Introduction

The self-assembly of block copolymers (BCPs) into a nanostructure with novel morphology and property has attracted an increasing interest as a new approach for materials science, chemical synthesis, and nanofabrication [1,2]. Recently, rod-coil block copolymers have received a great deal of attention since they offer an attractive strategy for the organization of many highly functional rod-like polymers such as helical biopolymers and conducting polymers with rigid π -conjugated backbones [3]. In particular, block copolymers containing conducting polymer segments, such as polyfluorene, poly(phenylene vinylene), have received much attention because of their prompt application to a wide variety of optoelectric devices. On the other hand, fluorinated block copolymers are of growing interest due to their unique properties such as very low surface energy and oil/water repellence, which cannot be achieved by corresponding non-fluorinated materials [4]. The unique properties of fluorinated polymer may be transferred to other polymeric materials by copolymerization.

Polymeric nanocomposites are commonly defined as a binary mixture of functional inorganic nanomaterials dispersed in a polymeric matrix. The stabilization of nanoparticles (NPs) with polymers

has been investigated by a number of groups [5,6]. Although innumerable research articles were shown in the literature for the self-assembly of BCPs and the morphological development of the hybrid films of BCPs and NPs [7-9], few works have been reported for the block copolymers of π -conjugated and fluorinated polymers which have potential applications to optical and microelectronics devices. In this work, semifluorinated BCP micelles are used as a template for composites to generate well-dispersed NPs with uniform size and shape without severe aggregation. Three different annealing modes of Au-loaded block copolymeric thin films were employed: in solvent vapor, in supercritical CO₂ at 70 °C and in a vacuum oven at 150 °C.

2 Experiment section

2.1 Synthesis of block copolymers by ATRP

The semifluorinated diblock copolymers poly(3-hexylthiophene)-b-poly(1H, 1H-perfluorooctyl methacrylate) (P3HT-b-PFOMA) were synthesized by atom transfer radical polymerization (ATRP) of FOMA using P3HT-Br as the macroinitiator in the mixed solvent of toluene and trifluorotoluene as described previously [10].

2.2 In-situ synthesis of gold nanoparticles and ordering of the prepared micellar thin film

The micellar thin film was fabricated by spin-coating at 700 RPM from the chloroform solution (1 wt%) of the BCP on a piece of freshly cleaved mica. The LiAuCl₄-loaded micellar solutions were prepared by adding 0.1 wt% of LiAuCl₄ into the pre-prepared copolymeric micellar solutions. The LiAuCl₄-loaded thin film on the mica was annealed in scCO₂ in a high-pressure reactor. After charging the sample, the reactor was sealed and pressurized at 13.8 MPa with carbon dioxide using a high-pressure syringe pump (ISCO-Model 2608) and the reactor was heated to 70 °C in a water bath for 12 h. The sample was taken for TEM analysis after depressurization by venting CO₂ from the top of the reactor. After annealing, the film was easily separated from the mica substrate by floating on water due to the strong affinity of water to mica. The film was transferred to a regular TEM copper grid having no supports. The LiAuCl₄-loaded thin film on mica substrate was also annealed in a vacuum oven at 150 °C for 24 h and examined with TEM analysis. For solvent vapor annealing, the thin film with gold or without gold was placed into a glass vessel with the reservoir of a fluorinated solvent, perfluoroalkanes - primarily compounds with 8 carbons (PF-5080) or trifluorotoluene (TFT). The temperature of the fluorinated solvent vapor was always kept at 70 °C. P3HT-*b*-PFOMA films were exposed to different solvent vapors for different periods to induce mobility and develop ordered nanostructures. After the vapor treatment, the samples were taken out from the vessel and dried in the air at room temperature.

2.3 Characterization

¹H NMR spectra were obtained in CDCl₃ and a mixed solvent of trichlorofluoromethane and CDCl₃ for the P3HT macroinitiator and the semifluorinated block copolymers, respectively using a JNM-ECP 400 (JEOL). The morphologies of the thin films were investigated by transmission electron microscope (TEM) using a Hitachi H-7500 instrument operated at 80 kV.

3 Results and discussion

3.1 TEM studies of nanostructured morphology

A new type of π -conjugated BCP of semifluorinated poly(fluorooctyl methacrylate) was synthesized by ATRP. ATRP yielded diblock copolymers with

well-defined molecular weights. The second block, PFOMA, is a semifluorinated polymer with several interesting properties of its own [11,12]. For this study, 4k of P3HT was used as a macroinitiator to produce P3HT_{4k}-*b*-PFOMA_{14k}. Nano-ordered microphase separation has been found in a rod-coil BCP film, similar to a conventional coil-coil BCP, induced by spontaneous self-assembly of each immiscible segment in which domains rich in one block are separated from domains rich in the other so as to minimize contact energy. In our work, the nanoscale morphology of the BCP in the solid-state was investigated using TEM for films cast from chloroform. Regioregular poly(3-hexylthiophene) forms a characteristic nanofibrillar morphology. TEM image of P3HT-*b*-PFOMA copolymer is shown in Fig. 1A, where nanofibrillar morphology is clearly evident, pointing to the prevalence of this type of supramolecular structure in P3HT based materials [13-15].

A control experiment was performed in order to assign the specific phases in the TEM image to P3HT and PFOMA blocks of the copolymer. The Fig. 1B shows the TEM image of as-spun asymmetric P3HT_{4k}-*b*-PFOMA_{14k} micellar films from chloroform after adding 50 wt% of the PFOMA homopolymer. It can be seen that the nanofibrils were changed to the densely packed shape with the addition of the PFOMA homopolymer into the block copolymer. Therefore, it is considered that the darker phase and lighter phase in the TEM images correspond to the major component, the PFOMA blocks and the minor component, the P3HT blocks, respectively. The electron density of semifluorinated PFOMA blocks could be higher than P3HT. The obtained nanofibrillar microstructure is the result of interplay between different driving forces of self-assembly (π -stacking versus phase separation).

The development of the surface morphology of P3HT-*b*-PFOMA copolymeric thin films was further investigated with annealing in PF-5080 and TFT solvent vapor, which are selective solvents for the PFOMA block,. When the samples are exposed to solvent vapor at 70 °C, the mobility is imparted to the system, as when the polymer is heated above its transition glass temperature (T_g), and the morphology would change. Therefore, it is interesting to investigate the process of morphology evolution under various solvent vapors. During

fluorinated solvent annealing, the PFOMA block absorbed more PF-5080 than P3HT due to the selective solubility of PF-5080 for PFOMA blocks. Hence, the mobility of PFOMA was larger than that of P3HT. The morphologies of polymer films with the same thickness (approximately 80 nm) but different annealing times were investigated (Fig. 2). After 4 h, the film displayed a featureless morphology, just like the as-cast film after PF-5080 vapor annealing as shown in Fig. 2A. An incomplete change was also observed in this morphology, indicating the PF-5080 vapor treatment for 4 h is not enough to reach in an equilibrium morphological state. However, upon longer annealing, P3HT nanofibrils and dark PFOMA aggregates are well developed. The morphology was developed to the dendrimer structure with longer nanofibrils after annealing in PF-5080 for 16 h (Fig. 2B). The as-cast thin film was also subjected to the TFT solvent vapor annealing. The development of the morphology of the micellar thin films in TFT vapor which has also preferential affinity for PFOMA blocks was investigated by TEM. After annealing in TFT solvent vapor environment for 4 h, no specific morphology was formed as shown in Fig. 2C. After 16 h of TFT vapor annealing, nanofibrillar morphology of P3HT_{4k}-b-PFOMA_{14k} was distinctly different (Fig. 2D). The nanofibrils were longer than that from PF-5080, isolated from one another, and were randomly oriented throughout the sample. All the branched longer nanofibrillar domains eventually form a networked morphology after annealing in TFT solvent vapor for 16 h. The formation of nanofibrillar structure of P3HT-b-PFOMA copolymers is undoubtedly dictated by the phase separation and crystallization of P3HT blocks [16,17]. The formation of quasi-one-dimensional objects such as nanofibrils indicates that the block copolymer self-assembles in a highly anisotropic way. Moreover, the phase separation between P3HT and PFOMA chains most probably takes place within nanoscale structure because P3HT and PFOMA segments are highly immiscible. The final nanofibrillar morphology must therefore be a compromise between the molecular organizations typical of each subphase.

3.2 Ordering of gold nanoparticles in nanodomains

For the preparation of ordered AuNP/polymer thin films, the copolymers were first dissolved in CHCl₃. The LiAuCl₄-loaded micellar solution were prepared by adding 0.1 wt% of LiAuCl₄ into the pre-prepared copolymeric micellar solutions. A freshly prepared aqueous solution of sodium borohydride was added slowly to the mixture with vigorous stirring. The color change from orange to dark purple evidenced the formation of AuNPs and the interaction with metal ions by sulfur atoms of P3HT. Torsi *et al.* has shown that conjugated polymers can stabilize inorganic nanoparticles by coordinating or forming complexes with the inorganic nanoparticles [18]. Furthermore, Ng *et al.* has demonstrated that sulfur atoms of polythiophenes can interact with metal ions [19]. Hence, it is assumed that the AuNPs are stabilized by the interaction of the sulfur atoms of poly(3-hexylthiophene)s with the gold surface. Fig. 3A shows the TEM image of the thin film spin-coated from the LiAuCl₄-loaded micellar solution of P3HT-b-PFOMA. It shows the nanowire morphologies in which the gray regions are the PFOMA phase in accordance with the higher electron density of the fluorinated blocks, the bright color of the P3HT phase is marked by dark dots which are gold nanoparticles resulting from the reduction of tetrachloroaurate. It is notable that the morphology of the micelles with NPs is similar to the micelles without the particles, from previous images (Fig. 1A). In the thin film, the average diameter of the AuNPs was calculated to be 8 nm. For phase development, the thin films were attempted to anneal under saturated PF-5080 at 70 °C, in a supercritical CO₂ environment at 70 °C, or thermally at 150 °C in a vacuum oven (Fig. 3). Each treatment imparts mobility to the BCP thin films, allowing them to reach their equilibrium morphology. The upper glass transition temperature of PFOMA is 58 °C. The high temperature provides sufficient thermal energy for the chains to reorganize as they try to reach thermodynamic equilibrium. Fluorine-containing polymers are highly solvophobic (lipo- and hydrophobic), i.e. they are insoluble in common organic solvents but are soluble in fluorinated solvents. This leads to easy phase-separation in BCP thin films as well as facile self assembly in organic solvents [4]. We also examined the morphological structures of the Au-loaded thin films upon annealing in scCO₂. Due to its high diffusivity and solubility for fluorous

polymers, it has been reported that scCO_2 annealing accelerates the ordering process of the block copolymers [20]. ScCO_2 can penetrate into fluorinated block copolymers and swell the fluorinated blocks selectively. All the experimental results shows branched, and eventually connected to other nanofibrils after the annealing. The length of the nanofibrils increased a little with pronounced branching. The gold nanoparticles were produced in the thin films of P3HT-b-PFOMA and dispersed in the P3HT phase. In the thin films, the average diameter of the gold nanoparticles was in the range of 9-11 nm after annealing.

4 Conclusion

π -Conjugated and semifluorinated diblock copolymers consisting of P3HT and PFOMA were synthesized by ATRP using the end functionalized P3HT as the macroinitiator. The diblock copolymers exhibited a range of densely packed nanofibrillar morphologies with variable degrees of interfibrillar order. The ordering is improved by solvent vapor annealing under PF-5080 and TFT, where the block copolymeric thin films show nanometer-scale nanofibrillar morphologies. It was also demonstrated that BCP micelles in thin films effectively act as a template to produce nanocomposites through complexation with gold precursors and annealing. The gold nanoparticles are stabilized by the interaction of the sulfur atoms of P3HTs with the gold surface and it dispersed in the P3HT phase. The length of nanofibrils increased a little with pronounced branching after thermal annealing, solvent annealing and scCO_2 annealing of the micellar films with Au NPs. Regioregular poly(3-hexylthiophene)/gold nanoparticle hybrid materials may find applications in single-electron tunneling studies as well as organic field effect transistor.

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5 Figures

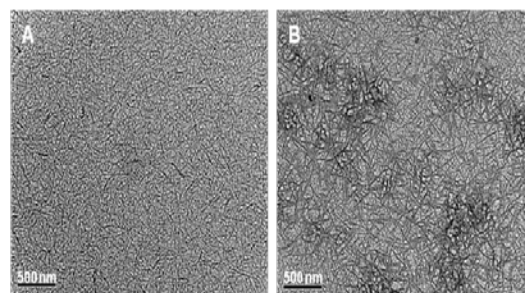


Fig. 1. TEM images the self-assemble structure of P3HT-b-PFOMA copolymeric thin films: (A) spin cast thin film, and (B) after adding FOMA homopolymer (50%)

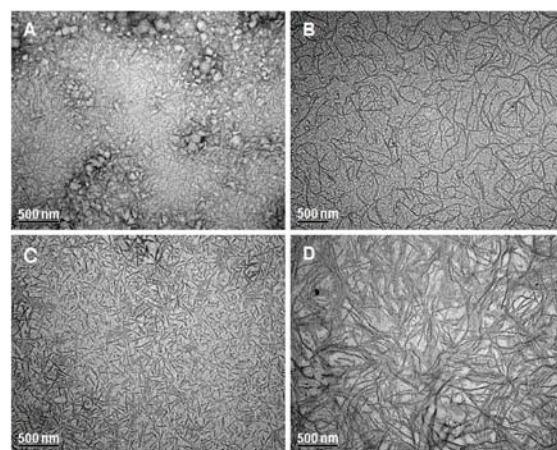


Fig. 2. TEM micrographs of P3HT_{4k}-b-PFOMA_{14k} thin films obtained after PF-5080 vapor annealing for (A) 4 h and (B) 16 h, and TFT vapor annealing for (C) 4 h and (D) 16 h.

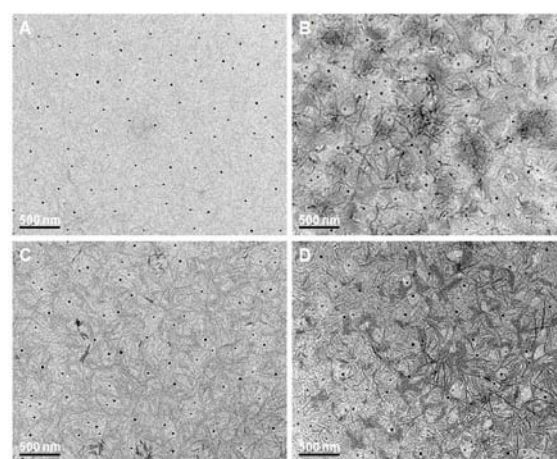


Fig. 3. TEM images of AuNPs produced in micellar thin films of P3HT-b-PFOMA: (A) spin-cast film from chloroform solutions, (B) after annealing in a vacuum oven, (C) after PF-5080 solvent vapor treatment and (D) after annealing in scCO_2

6 References

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