

Effect of nanoparticle surface functionality on microdomain orientation in block copolymer thin films under electric field



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ABSTRACT

The electric field induced microdomain orientations has been an interesting research topic. In this article, the effect of nanoparticle surface functionality on microdomain alignments in block copolymer/nanoparticle hybrid thin films was investigated with transmission electron microscopy experiments. The presence of gold nanoparticles influenced the microdomain orientation behaviors of block copolymer/nanoparticle thin films. The possibility for complete alignment normal to the substrate was illustrated by controlling electric field strength, concentration, and surface ligands of nanoparticles. This work provides basic and essential data to understand the properties and behaviors of emerging block copolymer/nanoparticle hybrid thin films.

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1. Introduction

The spontaneous formation of nanostructures *via* the molecular self-assembly of block copolymers (BCPs) has attracted increasing scientific interest due to the growing number of applications of nanopatterns [1]. The natural self assembly of BCPs into periodically ordered morphologies with a tens of nanometer scale offers an efficient means of fabricating nanomaterials [2,3]. Proposed applications include the construction of high-capacity data-storage devices [4], waveguides [5], quantum dot arrays [6], and nanoporous materials [7]. Although the self-assembly process is exceptionally efficient, it does not always produce the desired pattern. For example, lamellar and cylinder microdomains tend to orient parallel to the substrate rather than perpendicular where they would produce more useful structures [8]. To harvest the full potential of self-assembled BCPs, adaptable strategies are required to control and manipulate their spatial orientations, periodicity, connectivity, and long-range order [9]. Techniques that do not alter the chemistry on the molecular level, but rather use external stimuli such as temperature, mechanical shear, solvents, electric/magnetic fields are indispensable [10]. In any case, understanding physical and chemical properties of BCPs is still one of the most active research areas in material science.

Recently, functional materials that rely on the combined properties of soft materials, BCPs and the functionality of inorganic additives such as nanoparticles (NPs) have attracted considerable interests. The homogeneous addition of inorganic NPs into BCPs is potentially an effective route for the fabrication of functional hybrids such as photonic band gap materials [11], highly efficient catalysts [12], ultrasensitive sensors [13], and storage media [14]. The microdomains of BCPs provide a robust template within which the inorganic NPs can be accommodated [15]. In addition, the precise control of both size and spatial location within the BCPs is a prerequisite for most applications. Therefore, the use of these emerging composite materials requires understanding of the profound structural, rheological, and physical properties of BCP/NPs hybrids due to the introduction of NPs into the BCP matrix [16–20].

Among various properties of BCP/NPs, the interaction and behavior of BCP/NPs hybrids under external electric fields is one of the least unknown topics. The interaction of an electric field with a dielectric material is well understood, since Swan first investigated the influence of electric fields on the surface of polymers or viscous liquids [21]. For BCPs, electric fields have been proven to be an effective mean to control the microdomain orientation in BCP thin films [22–27]. The driving force for these processes is the orientation-dependent polarization in a material having a dielectric interface. The electric field aligns interfaces separating two dielectric bodies parallel to the electric vector, thus minimizing the moment of electrostatic forces exerted onto the interface [28].

Even if numerous theoretical and experimental investigations on the microstructures and behaviors of BCP/NPs hybrids have been

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reported, few systematic studies have been conducted that deal with the interaction of BCP/NPs composites with external electric fields. Yan and Böker have reported the large-scale assembly of NPs in BCP templates [29] and theoretical examination for dynamic behavior of BCP/NPs microstructure under electric fields [30]. However, the realization of the full potential of BCP/NPs materials requires controlling the microdomain ordering and orientation to a desired direction. Therefore, in this study, gold (Au) NPs with tailored surface ligands were incorporated into poly(styrene)-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) matrix to investigate the effect of NPs surface functionality on microdomain alignment along the field direction under external electric fields. The surface ligand effect was highlighted using cross-sectional transmission electron microscopy observations (TEM). The effect was also demonstrated as a function of block copolymer compositions. This study provides basic and fundamental data for better understanding of electric field induced microdomain orientation in BCP/NPs hybrid thin films.

2. Experimental

2.1. Materials

Two types of poly(styrene)-*b*-poly(2-vinylpyridine) BCPs having the same blocks and different compositions, PS-*b*-P2VP (Lamellar) (number average molecular weight: M_n , PS = 25 kg/mol, P2VP = 23 kg/mol, $M_w/M_n = 1.08$) and PS-*b*-P2VP (Cylinder) (number average molecular weight: M_n , PS = 32 kg/mol, P2VP = 12 kg/mol, $M_w/M_n = 1.07$) were purchased from Polymer Source (Quebec, Canada) and were used without further purification. Common solvents, toluene and tetrahydrofuran (THF) were dried using a common method. Gold NPs were prepared by established procedures [31]. For example, polystyrene-functionalized gold NPs (Au(PS)), with an average gold diameter of 4 nm, were prepared according to the Brust-Schiffrin method, by the reduction of hydrogen tetrachloroaurate with sodium borohydride using polystyrenethiol as a ligand [31]. The molecular weight of the PS ligand was 1 kg/mol, and the density of the Au(PS) was 19.3 g/cm³. Also, Au NPs were functionalized with a mixture of hydrophobic ligands by ligand exchange to prepare dodecanethiol-covered Au NPs (Au(DDT)) [32–34].

2.2. Preparation of BCP/NPs hybrid thin films

Poly(styrene)-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) was dissolved in THF at room temperature. THF is a good solvent for both PS and P2VP. Then 1 vol% of NPs was added to the solution with mild stirring. BCP/NPs hybrid thin film was spin-coated onto a silicon wafer at 2000 rpm for 60 s from a BCP/NPs mixture solution. The hybrid thin films were then dried under ambient conditions. Subsequently, the dried films were thermally annealed at 170 °C, considerably above the glass transition temperature of both blocks for at least 48 h before exposure to an electric field.

2.3. Application of electric field

Fig. 1 shows a schematic diagram describing the apparatus in which the electric field was applied. A silicon wafer, spin coated with a hybrid thin film, served as one electrode, and a soda-lime glass coated with a thin layer of gold (20 nm) and chromium as the adhesion promoter (5 nm) served as the second electrode. A rectangular well was etched in the glass slide by immersion in buffered HF using a poly(methyl methacrylate) mask. The electrode spacing was controlled by varying the etching time: 0.2 μm/min. In this geometry, the dominant gradient in the electric field occurs

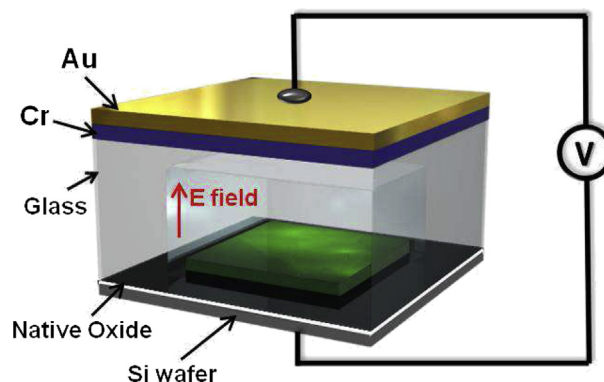


Fig. 1. Schematic diagram of experimental apparatus.

across the air/nanocomposite film interface. A voltage was applied, and the assembly was heated for 12–24 h at 170 °C, considerably above the glass transition temperature of the two blocks. The assembly was then quenched to room temperature to freeze the pattern. After each experiment, the upper glass electrode was mechanically removed.

2.4. Instrumentations

Transmission electron microscopy (TEM) experiments were performed with a JEOL 200CX TEM operated at an accelerating voltage of 200 kV. First, the thin BCP/NPs films were spin coated onto a silicon wafer having a 250 nm thick silicon oxide layer. The oxidized silicon layer was etched with a 5% hydrofluoric acid (HF) aqueous solution. The separated polymer thin film was retrieved using a copper grid and examined using TEM. To prepare cross-sectional TEM specimens, a thin layer of carbon was evaporated onto the film surface before embedding in epoxy resin to prevent the diffusion of the epoxy resin into the hybrid thin film. The thin film was then embedded in an epoxy resin and cured at 60 °C for 18 h. The films were removed from the substrate by dipping into liquid N₂. Ultrathin sections (60 nm) were collected at room temperature using a Leica Ultracut Microtome, equipped with a diamond knife. The thin sections were exposed to iodine vapor for 30 min to enhance the contrast.

3. Results & discussion

To examine the effect of the NP surface functional group on the microdomain alignments of BCP under an electric field, two types of surface ligands, PS and dodecanethiol (DDT), were introduced on Au NPs. While the PS ligand shows a selectively favorable interaction with the PS domain, the DDT ligand provides a similar affinity to both blocks. The molecular weights of PS and DDT ligands are significantly different. But, the radius of gyration for 1 kg/mol PS ligand is approximately 1 nm, which is comparable with the molecular size of DDT. Thus the effect of molecular size can be negligible. In addition, the areal density of 1 kg/mol PS ligand on Au NP is approximately 2 chains/nm². In this range, it can be inferred that the Au NPs were entirely covered with PS ligands as Kramer and co-workers reported in the previous research [35]. It would also become clear that the PS covered Au NPs primarily located in the center of PS domains [35]. In order to investigate the BCP composition effect, two types of BCPs, PS-*b*-P2VP (L) (Lamellar; PS:P2VP = 52:48) and PS-*b*-P2VP (C) (Cylinder; PS:P2VP = 71 : 29), were compared. BCPs with a large dielectric constant difference (PS:2.5, P2VP:4.6@10³ Hz) were selected to closely observe the microdomain orientation behavior [36].

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