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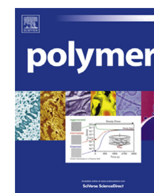

Ruthenium staining for morphological assessment and patterns formation in block copolymer films

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ABSTRACT

The selective staining by ruthenium tetroxide (RuO_4) was used in combination with Atomic Force Microscopy and calcination to discriminate and assign microphases at the surfaces of films of complex polymer systems. This paper evaluates this technique on thin films of polystyrene-*b*-polylactide (PS-*b*-PLA) and polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) and demonstrates its efficiency on complex thin film of binary blend of PS-*b*-PMMA and PLA. This method overcomes difficulties in the interpretation of AFM images by assigning PS microphase. In addition we show that this methodology could yield nanostructured inorganic materials with tunable structures such as perforated layers or nanowires that could find potential applications in the fabrication of high specific surface area Ru oxide-based materials.

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1. Introduction

Intermittent-contact (IC) mode atomic force microscopy (AFM) is a widely used technique for imaging nanostructured surfaces and is particularly useful for the study of block copolymer (BCP) thin films. The consideration of height and phase images leads respectively to topographical information and domain discrimination at the surface [1–8]. However, AFM imaging and analysis of thin films of block copolymers can be difficult due to low contrast or contrast inversion problems. As a result, the discrimination and assignment of specific microdomains of the block copolymer can be quite challenging in certain systems (e.g., in cases where the blocks have similar mechanical properties). AFM imaging and analysis of thin films of complex systems, such as ternary blend or multiblock polymers, is even more challenging. Such problems could also originate from the chosen experimental scanning parameters (e.g., amplitude of free oscillation, set-point amplitude ratio and tip–sample interactions) [1,9–12]. While these difficulties can be avoided by careful choice of the experimental parameters, this is usually time-consuming [1–5,13]. Contrast enhancement can also be realized by swelling in selective solvent vapors [14] or by removing one polymer from the surface but this can lead to the delamination of the film [15].

Here we demonstrate an approach that overcomes these difficulties through selective component staining by ruthenium tetroxide (RuO_4). RuO_4 effectively stains polymers such as polystyrene [16–18], poly(ethylene oxide) and poly(vinyl pyridine) but does not stain others such as poly(methyl methacrylate) [19]. Selective RuO_4 staining is commonly used in transmission and scanning electron microscopy to enhance contrast in various polymer-containing samples and have been already reported by several groups [20–27]. We have extended this selective staining by RuO_4 to an AFM method that allows for enhanced image contrast of polymers. The efficiency of this technique to distinguish polymers microdomains and simplify their assignment is firstly illustrated for thin films of polystyrene-*b*-polylactide (PS-*b*-PLA) and polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) block polymers and then applied for the binary blend of PS-*b*-PMMA and PLA. It is shown that staining is a useful approach not only for discrimination but also for identifying one polymer over the others.

Calcination of stained diblock copolymer can be used to yield a replication and definitive localization of the PS domains. This calcination removes the polymer, leaving behind a pattern of ruthenium oxide based nanostructures. As a further extension, these nanostructures could have a great interest. Due to its electrical and electrochemical properties, RuO_2 is the subject of intense studies for electrochemical energy storage/conversion devices. For example, due to its high capacitance, RuO_2 is a good candidate for supercapacitors [28] and efforts have been made to produce such materials with high specific surface areas [29]. There is no doubt

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that this methodology, which generates nanostructured RuO_2-based materials, could also be applied in this field.

2. Experimental

Cylinder-forming block copolymer PS-*b*-PMMA was purchased from Polymer Source and has a total molecular weight of 101 kg.mol^{-1} and a PMMA volume fraction of 30%. Cylinder-forming PS-*b*-PLA was provided by Prof. Marc Hillmyer at the University of Minnesota and has a total molecular weight of 90 kg.mol^{-1} and a PLA volume fraction of 34%. PLA homopolymer has a molecular weight of 16 kg.mol^{-1}. $RuCl_3•3H_2O$ and NaOCl were purchased from Sigma Aldrich and used as received.

PS-*b*-PLA and PS-*b*-PMMA were dissolved in chlorobenzene (20 mg.ml^{-1}) and deposited by spin coating on Si substrates that were previously cleaned and treated by 1/1/50 $HF/HCl/H_2O$ solution. As the spin coating process can only lead to vitrified films with poor long-range order, the films were exposed to tetrahydrofuran (THF) vapor for times ranging between 5 and 10 min in a 150 ml closed vessel containing 10 ml of THF at 20 °C to reorganize the block copolymers. For the binary blends, a 10 mg/ml PLA solution was prepared using acetone and PS-*b*-PMMA was dissolved in toluene to prepare a 20 mg/ml solution. The PS-*b*-PMMA solution and PLA solution were then mixed together to obtain a solution with 5w/w % PLA in the binary blend (1 mg/ml PLA solution). Thin films of this binary blend of PS-*b*-PMMA block copolymer and PLA homopolymer were prepared by spin-coating, exposed to 5 min. THF vapor and examined by AFM. Compared to previous published results [15], the ratio of the chamber volume versus THF volume was smaller here, allowing for shorter annealing time. Of course, the solvent vapor pressure is one of the most important parameters that govern the swelling of the film and thus its final morphology. However in this type of device, it has been shown that annealing chamber size and other parameters such as temperature influence the steady state vapor pressure and the time it takes to achieve this pressure [30]. Films thicknesses ranged between 50 and 100 nm and were measured by imaging a scratched area in AFM tapping mode.

Ruthenium tetroxide staining was performed by exposing the thin films to RuO_4 vapor for 10 min in a 150 ml closed vessel at 20 °C. The RuO_4 staining solution was prepared by mixing 20 mg of $RuCl_3•3H_2O$ and 1 ml of 10 w/v % NaOCl solution following the procedure described in the literature by Brown and Butler [31]. Finally, the thin films were calcined at 350 °C for 10 min to create an inorganic ruthenium oxide material mimic of the original pattern.

For comparison purposes, PLA domains were eliminated by hydrolysis by immersing the thin films into a 0.5 M NaOH solution with 40 v/v % methanol/water for 10 min followed by rinsing with a 40 v/v % methanol/water solution [15]. This selective PLA removal enhances topographical contrast. Similarly, the PMMA domains could be extracted by exposing the sample to UV light with wavelength of 254 nm for 4 h followed by rinsing with concentrated acetic acid [32].

AFM images were collected using a Nanoscope IIIA from Digital Instruments in tapping mode. Height and phase images were simultaneously recorded. Silicon cantilevers with a nominal drive frequency of approximately 300 kHz were used. Scanning Electron Microscopy (SEM) was carried out on a Hitachi S4200 device combined with an Oxford analyzer controlled by Link Isis software. The electron gun was equipped with a field emission electron source and was operated at 5 keV.

3. Results

As-spun films of PS-*b*-PLA exhibited a disorganized but microphase separated morphology. AFM height and phase images with identical scale of as-spun PS-*b*-PLA films are shown in Fig. 1a, d, after staining in Fig. 1b, e and after PLA hydrolysis in Fig. 1c, f. Discrete domains, forming apparent depressions, were observed within a continuous matrix. Most features were circular but some are wormlike. The morphologies presented in Fig. 1 were compared using 2D-power spectral density (PSD) analysis (see Supporting Information S1). PSD analysis could not allow describing precisely the domains size and spacing but helps to follow if deep modification of the structure happened during staining and during hydrolysis.

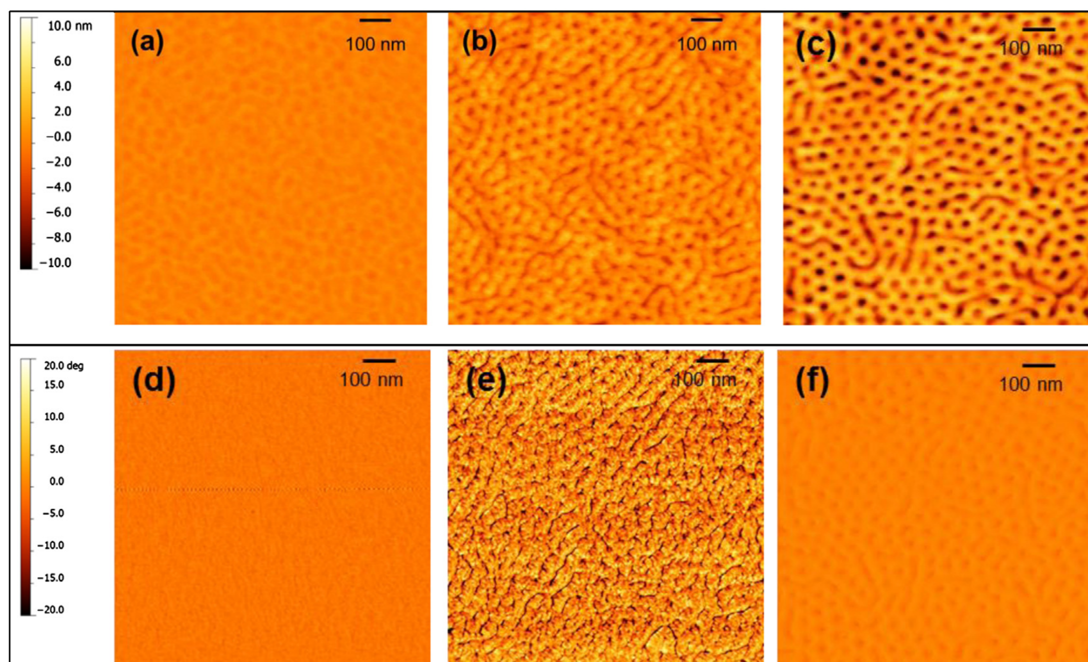

Fig. 1. (1 μm × 1 μm) AFM height (top) and phase images (bottom) of: as-spun PS-*b*-PLA thin film (a, d); after 10 min staining (b, e); after PLA hydrolysis without any staining (c, f).

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