Colloids and Surfaces A: Physicochem. Eng. Aspects 444 (2014) 217–225

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Solvent induced nanostructure formation in polymer thin films: The impact of oxidation and solvent

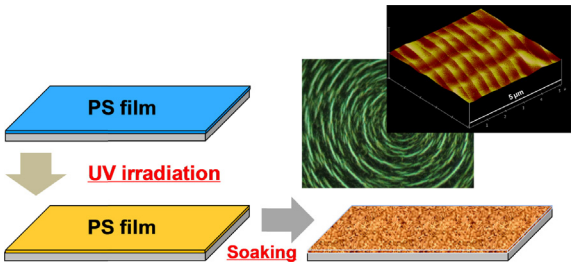
Takuya Kubo[a,*], Jisun Im[b], Xin Wang[c], James E. Whitten[b], Koji Otsuka[a], Mingdi Yan[b]

[a] Graduate School of Engineering, Kyoto University, Katsura Nishikyo-ku, Kyoto 6158510, Japan
[b] Department of Chemistry, University of Massachusetts Lowell, 1 University Ave., Lowell 01854, MA, USA
[c] Molecular & Cell Biology Division, Life Technologies, Eugene 97402, OR, USA

HIGHLIGHTS

- We developed self-organized polystyrene film by UV exposure and soaking in solvents.
- The results provide the effects of crosslinking and oxidation for nanostructure.
- XPS results showed the impact toward the oxidation parts by solvents.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 June 2013
Received in revised form
16 December 2013
Accepted 24 December 2013
Available online 3 January 2014

Keywords:
Polystyrene films
UV-irradiation
Oxidation
Nanostructures

ABSTRACT

Polystyrene (PS) films, upon deep UV exposure, readily formed nanostructures when soaking in a solvent. In this study, we provide compelling evidence confirming the critical roles of oxidation and solvent for the nanostructure formation. When the irradiation was carried out in argon, no structure could be generated on the films. Solvent is another critical parameter. Ordered concentric circular structures formed when the UV-irradiated PS films were soaked in an aromatic solvent such as toluene, benzene, and xylene. Addition of *n*-heptane to toluene reduced the size of the circles. The concentric circular structures disappeared when 0.1% methanol was added to the soaking solvent toluene. X-ray photoelectron spectroscopy (XPS) showed that the percentage of O-containing products decreased with increasing amount of added methanol, indicating that the polar solvent prevented the structure formation by removing the oxidation products from the films.

1. Introduction

Nanostructured organic or inorganic thin films have demonstrated increasing potential in applications such as electronics, biomedical devices, and nanomaterial synthesis [1–3]. With the rapid development in new nanofabrication tools and lithography processes, significant progress has been made where well-defined and ordered nanostructures can be created on a large scale. An alternative approach to nanostructure formation relies on molecular self-organization whereby nanoscale domains are formed when triggered by external stimuli. Polymers are excellent precursors for creating nanoscale structures by self-assembly. Polymers, being soft materials, can be readily manipulated by a variety of physical and chemical stimuli. For example, block copolymers undergo phase separation to form periodic structures of 10–100 nm, controlled by the size of the polymer blocks [4–7].

Self-organized wrinkle structures are another example of polymer self-organization formed as a result of the instability in polymer thin films [8,9]. For instance, bulk samples or thin films of poly(dimethylsiloxane), upon exposure to oxygen or argon plasma, form wavy surface structures due to the crosslinked stiffer outer layer which spontaneously wrinkles to relieve the strain [10–15].

* Corresponding author. Tel.: +81753832448.
E-mail address: kubo@anchem.mc.kyoto-u.ac.jp (T. Kubo).

0927-7757/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfa.2013.12.052

Guvendiren et al. created surface patterns in poly(hydroxyethyl methacrylate) hydrogel films by combining the solvent-induced gel swelling and the buckling effect due to the modulus gradient through film depth [16]. Polystyrene (PS) thin films have been studied extensively where various wrinkle structures were induced mechanically by, for example, placing a drop of water on freely floating PS thin films, or melting a semicrystalline polymer underlayer [17]. The wrinkle structures can also be created by toluene vapor exposure of, for instance, UV/ozone-treated PS thin films or a relatively thick PS layer (0.1–1 μm) through a thin titanium membrane deposited on top of the PS layer [18].

We have previously reported the formation of self-organized PS structures by soaking UV-treated PS thin films in toluene [19]. UV irradiation generates free radicals which undergo crosslinking and oxidative degradation in the presence of oxygen [20–29]. We postulated that the structure formation was a result of swelling and self-assembly when the UV-irradiated PS films were treated with toluene. In this paper, we investigate the parameters that control the structure formation. The addition of free radical inhibitor and the impact of oxidation and the soaking solvent were studied with regard to the structure formation. X-ray photoelectron spectroscopy (XPS) was used to further help elucidate the structure formation.

2. Experimental

Solvents used in this study and *p*-*t*-butylcatechol (TBC) were purchased from Sigma–Aldrich. Monodisperse PS (MW 979,800) was purchased from Scientific Polymer Products Inc. (Ontario, NY). Silicon wafers with a 35 Å native oxide layer were purchased from WaferNet Inc. (San Jose, CA). Surface images were obtained on an atomic force microscope (Nanoscope III, Veeco) and an optical microscope (Olympus BHM). Film thicknesses were measured on a Gaertner Model L116A ellipsometer (Gaertner Scientific Co.) with a He/Ne laser (632.8 nm, 2 mW, Melles Griot) at an incident angle of 70° in the manual mode. The real and imaginary parts of the refractive index of the silicon wafer were 3.870 (N_s) and −0.018 (K_s), respectively. The refractive index (n_f) of PS, 1.592, was used to calculate the thickness of PS films.

XPS spectra were acquired using a VG ESCALAB MK II photoelectron spectrometer with a base pressure in the 10^{-10} torr range. The operating pressure was in the range of $1–3 \times 10^{-9}$ torr. MgKα X-rays (1253.6 eV) were used, and the kinetic energy of the photoelectrons was measured with concentric hemispherical analyzer with pass energy of 20 eV and at a take-off angle of 90°, defined as the angle between the surface plane and the perpendicular to the entrance of the high voltage lens of the analyzer. Curve fitting for C1s peaks was carried out using the "Avantage" software. Because of incomplete charge compensation of ejected photoelectrons, some sample charging occurred, resulting in artificially high binding energies. The spectra were corrected by shifting them by the amount necessary to set the binding energy of the C1s peak of PS to its correct value of 284.7 eV [30].

Preparation of PS films: Silicon wafers were cut with a diamond pen into 1 × 1 cm pieces and were cleaned by sonication in 2-propanol for 30 min and dried under a stream of nitrogen. PS solutions were prepared at 25 mg/mL in toluene. For the study on the impact of free radical inhibition, PS solutions were prepared at 22.5 mg/mL in toluene containing 0 to 1% TBC. The polymer solution was spin-coated onto the cleaned wafer at 2000 rpm for 60 s. The films were then irradiated with a 450 W medium-pressure Hg lamp (Hanovia) at ambient condition for 20 to 60 min and soaked in the solvent for 12 h. For the study on the impact of oxidation, the sample was placed in a quartz flask and purged with argon before subjecting it to irradiation and solvent extraction. For the vapor exposure experiment, UV-irradiated PS films were placed in a covered glass dish saturated with toluene vapor. The surface structure was imaged continuously using an optical microscope equipped with a digital camera. The films were subjected to toluene vapor for a total of 24 h and were then immersed in toluene and dried.

3. Results and discussion

3.1. Impact of crosslinking density, oxidation, and solvent exposure on structure formation

In a previous study, we observed ordered concentric circular structures by exposing PS thin films to UV followed by soaking in toluene [19]. Without soaking in toluene, the films remained smooth and no structures were formed just by UV irradiation. Others have used UV/ozone treatment and toluene vapor exposure to generate wrinkle structures on PS films [31]. To compare the differences in the structure formation between vapor exposure and solvent soaking, the UV-irradiated PS films were exposed to toluene vapor for 24 h. The optical image shows spoke structures on the film (Fig. 1a), similar to those reported in the literature [31]. The sample was then soaked in toluene, and the image was taken again. The spoke structure disappeared, and instead, concentric circular structures were observed (Fig. 1b). These structures are similar to those formed by directly soaking the UV-irradiated PS in toluene (Fig. 1c), although the spacing of the circles and the height of the structures were smaller. The concentric circular structures did not change even after the films were subsequently soaked in several solvents including water, acetone, heptane, and xylenes. These observations suggest that the concentric circular structures obtained by soaking in toluene are stable, whereas those by vapor exposure were not. The results further suggest that the interactions of toluene with the UV-irradiated PS films in the liquid phase are much stronger than in the vapor phase.

In this study, we examine in detail the effect of crosslinking density, oxidation, and soaking solvent on the structure formation. Crosslinking occurs via the combination of free radicals generated by UV irradiation of the polymer [20]. To investigate the effect of the crosslinking on the structure formation, TBC, a free radical inhibitor, was added to the polymer. The expectation was that TBC would inhibit free radical formation and, therefore, decrease the crosslinking density in the film. In the experiments, PS solutions in toluene containing varying amounts of TBC were spin-coated on silicon wafers, and the films were subjected to UV irradiation for 60 min with a 450 W medium-pressure Hg lamp. After soaking in toluene and drying with a stream of nitrogen, the films were examined under an optical microscope. Without TBC, concentric circular structures were observed throughout the film (Fig. 2a). As the concentration of TBC increased, the spacing between the circles decreased and the structures became less pronounced (Fig. 2b and c). For samples with 1.0% TBC added, most of the film was removed after soaking in toluene (film thickness was less than 2 nm by ellipsometry), and no structures were observed (Fig. 2d). These results indicate that TBC effectively reduced the free radical concentration and, thus, the crosslinking density of the films. The results further confirm that crosslinking is necessary for the formation of the concentric circular structures.

The effect of oxidation was next studied. Two samples were prepared in the same manner except that the UV exposure was carried out in argon for one sample and in air under ambient conditions for the other. Although the concentric circular structures could be clearly seen on the film prepared in air (Fig. 3a), the structures were absent on the film prepared in the argon atmosphere (Fig. 3b). It is known that PS undergoes oxidation under extensive UV exposure in air [20]. The fact that no structures were formed