Photocatalytic printing of inorganic nanopatterns via poly(styrene-block-carbosilane) copolymer thin films on titania substrates†

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Well-defined, ordered arrays of nanoscale depressions were obtained in linear-brush-type polystyrene-block-poly(carbosilane) (PS-b-PCS) diblock copolymer thin films by acetone vapor annealing and silica nanodot arrays were directly obtained from such thin films deposited on a titania substrate by one-step exposure to UV light as a result of transformation of the PCS units to silica, driven by the photocatalytic activity of titania concurrent with removal of the organic matrix.

Numerous fabrication methods have been reported to generate patterned surfaces with regularly sized and spaced features on the nanometer scale.3,5 In order to generate nanostructured surfaces, conventional top-down lithographic approaches with electron-beam, interference, or X-ray lithography can be employed, although this is often not cost effective. Alternatively, bottom-up self-assembly techniques can be utilized to produce well-defined, ordered nanopatterns.3 In particular, block copolymer systems are attractive candidates due to their ability to self-assemble into a variety of nanoscale periodic morphologies, which can be further used as templates for the fabrication of nanodots and nanowires4,5 or as photoresists for pattern transfer to underlying substrates.6

While much effort has been devoted to the use of traditional linear block copolymers, diblock copolymers consisting of a linear block and a rod (or a branched) segment have attracted less attention as a tool for nanofabrication.7 However, a highly branched block may lead to particularly rapid nanophase segregation. Solvent-induced ordering has been used to produce ordered nanodomain morphologies with controlled orientation in block copolymer thin films.9 Although the preparation process usually leads to the formation of metastable structures that do not represent a melt equilibrium, such structures often exhibit high regularity and may be of particular interest for patterning applications.

Here we report on the self-assembly behavior of a novel diblock copolymer consisting of a linear polystyrene (PS) block and a highly flexible, brush-like poly(carbosilane) (PCS) block in a thin film geometry. Silicon-containing block copolymers offer additional opportunities for the creation of functional nanostructured materials.10 To our knowledge, there has been limited success in gaining control over the morphologies of this type of block copolymer. A schematic representation of the molecular architecture of PS-b-PCS is given in Fig. 1 (see detailed structure in Fig. S1†). The linearly-grafted carbosilane block unit was obtained by the grafting reaction of dimethyl(undec-10-enyl)silane (DMUS), an AB-type monomer, on a low molecular weight polybutadiene block (PBD) of a polystyrene-block-poly(1,2-butadiene) diblock copolymer (PS-b-PBD), which was synthesized by means of anionic polymerization.11,12 The comb block was prepared in a controlled manner via the Slow Monomer Addition (SMA) synthetic strategy (see ESI†).13,14 The reaction conditions employed were the same as for the linear-hyperbranched systems previously published, and the size of the brush-like block was analogously controlled by the monomer/core ratio.12 A PS325-b-PCS104 linear-brush-like diblock copolymer with a weight fraction of 31 wt% for the PCS block (including the short PBD-backbone) was used for the investigation. The comb PCS block showed a low Tg value of −43 °C, while the PS block exhibited a Tg of 93 °C. The detailed synthesis of PS325-b-PCS104 is given in the ESI.† Solvent annealing was used to control the orientation and lateral order of the microphase-separated domains. The resulting ordered nanoscale depressions formed in the PS-b-PCS thin films were employed to produce an inorganic nanopattern by exposing the thin films on a titania substrate to UV light.

At this step, transformation of PCS domains into silica nanoparticles due to the photocatalytic activity of the underlying titania substrate and removal of the organic matrix were simultaneously achieved. The spatial distribution of the silica domains on the surface was conserved. The overall scheme for generating such nanostructures is illustrated in Fig. 1.

The PS-b-PCS was dissolved in toluene with a concentration of 1 wt%. Titania substrates were obtained by spin-coating titania sol–gel precursor solution prepared by adding concentrated HCl (37%, 0.12 g) into isopropanol (2.5 mL) containing titanium tetra(isopropoxide) (TTIP, 0.37 g) on silicon wafers. Then PS-b-PCS thin films were prepared by spin-coating a toluene solution of the polymer onto the titania substrates at
2000 rpm for 60 s. The film thickness was \( \sim 40 \) nm determined by a surface profiler. The spin-coated films were exposed to five different solvent vapors (acetone, tetrahydrofuran (THF), toluene, benzene, CHCl_3) in closed vessels at room temperature (\( \sim 22^\circ C \)). After a certain exposure time (1–48 h), the samples were removed to ambient atmosphere and immediately dried. The samples were irradiated with UV light at 254 nm for 24 h to induce a transformation of PCS units to silica as well as to remove the PS matrix. The film morphology was characterized by atomic force microscopy (AFM, Dimension 3100) and field emission scanning electron microscopy (FESEM, LEO 1530 'Gemini'). The chemical composition of the final structure was characterized with a VG ESCA2000 X-ray photoelectron spectrometer using an Mg/Al source.

The as-cast PS-b-PCS thin films show a disordered, worm-like pattern (Fig. 2a) due to rapid solvent evaporation, allowing the chains insufficient time to rearrange to attain an equilibrium morphology. During the exposure to saturated solvent vapors, the selectivity and quality of solvent vapors for the constituent blocks are crucial for the pattern formation of PS-b-PCS films. We have tested several common solvents for solvent annealing, such as acetone, THF, toluene, benzene, and CHCl_3. Among them, acetone is a good solvent for PCS blocks but a poor solvent for the PS block, while all the other solvents used in this study are good solvents for PS blocks. It was found that an ordered microphase-separated pattern could only be obtained when acetone was used to treat the PS-b-PCS films. Upon exposure to acetone vapor, the PCS microdomains were swollen by acetone and the strong non-favorable interactions between PS and PCS blocks led to further microphase separation. This indicates that the mobility of the minor fraction, the PCS block, has a critical effect on the formation of an ordered microphase-separated pattern. When annealed in saturated acetone vapor for 5 h, the films transformed to a well-ordered array of the depressions (Fig. 2b). A depression size of \( \sim 20.2 \) nm, an interval of \( \sim 22.4 \) nm and a depth of \( \sim 1.1 \) nm (Fig. S2\textsuperscript{a}) were ascertained from the AFM image. Considering the volume ratio of 31% of the PCS segment, it is concluded that the darker areas represent the PCS nanodomains. The morphology is considered to consist of vertically aligned PCS cylinders in a PS matrix for the film thickness ranges used in this study (typically of the order of \( \sim 40 \) nm). Prolonged exposure to acetone vapor (48 h) further improved the lateral order and uniformity of nanoscale depression arrays (Fig. 2c). A quasi hexagonal order was
obtained, as verified by a magnified view, together with an FFT image (see Fig. S2†). A depression size of ~20.2 nm, an interval of ~22.4 nm and a depth of ~1.1 nm were ascertained from the sectional analysis. The corresponding phase contrast image is shown in Fig. 2d. Since PCS has a lower modulus than the PS chain at room temperature, PCS appears darker in the phase contrast images. The FESEM image at low magnification shows that the ordered array of nanoscale depressions covers a wide area of the surface, as evidenced in Fig. 3.

It has been reported that titania photocatalysts are capable of oxidizing silicon-containing organic compounds adsorbed on the surface of SiO2.15 Upon UV exposure, free radicals and activated species generated in situ from the combination of atmospheric oxygen and UV light can be used to remove organic polymer.16 When the films deposited on titania substrates were irradiated by UV light, the surface morphology of the films drastically changed into inorganic nanopatterns. Fig. 4(a) shows the AFM image of thus formed silica nanodots with an average height of ~0.9 nm and diameter of ~20.7 nm after exposing the ultrathin PS-b-PCS film with nanoscale depressions to UV light. For comparison, silica nanopatterns were not generated by the same experimental protocol on a Si wafer (data not shown), indicating that the photocatalytic activity of titania is a crucial factor to obtain silica nanostructures. The observed surface structures after UV irradiation were not removed by washing with organic solvents, indicating that these inorganic species were generated via a chemical transformation of the parent polymer. XPS measurements were carried out to identify the chemical nature of the silica nanodots. Characteristic peaks of Si were clearly observed from the high resolution S2p and O1s spectra in Fig. 4(b) and Fig. S3,† respectively. The peaks at ~103.0, ~102.0, and ~101.1 eV in Fig. 4(b) are attributed to SiO2, SiO, and SiO2 moieties, respectively. From the results, one can conclude that the silica nanodots are mainly composed of SiO2 with trace portions of SiO or SiO. It is clearly observed that silica nanodots retain the original spatial order and distribution of depressions on the surface of PS-b-PCS films. It is assumed that a higher silicon content would result in a larger size of silica nanodots. Such a photocatalytic printing protocol demonstrated by this study may represent a general route to fabricate diverse silica nanostructures with controlled morphology, using PS-b-PCS block copolymers with tailored architectures.

In summary, a simple pathway to well-defined linear-brush PS-b-PCS block copolymer thin films with ordered nanoscale depressions was developed by solvent vapor annealing of as-cast PS-b-PCS thin films. The nature of the solvent used for annealing was shown to control nanopattern formation. Only acetone vapor led to ordered array of nanoscale depressions in PS-b-PCS thin films. Subsequent UV treatment of such films led to pure silica nanodot arrays with their spatial distribution on the surface conserved, as a result of simultaneous photocatalytic performance of the underlying titania substrate and degradation of the PS matrix. The experimental methodology demonstrated in this work opens up a facile way to fabricate a broad range of inorganic or composite nanostructures.

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Notes and references