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Facile Approach to Patterned Binary Polymer Brush through Photolithography and Surface-Initiated Photopolymerization

Xinyan Jia,[†] Xuesong Jiang,[*,†] Rui Liu,[‡] and Jie Yin[*,†]

School of Chemistry & Chemical Technology, State Key Lab of Metal Matrix Composites, Shanghai Jiao Tong University, and National Engineering Research Center for Nanotechnology, Shanghai 200240, People's Republic of China

ABSTRACT Taking advantage of the photobleaching and co-initiating properties of the dendritic thioxanthone (TX) photoinitiator, we developed a general and facile approach to fabricate patterned binary polymer brushes by combining photolithography and surface-initiated photopolymerization (SIPP). The dendritic TX photoinitiator monolayer was immobilized covalently on a silicon slide surface, followed by photobleaching through a mask. The resulting slides could initiate photopolymerization of methyl methacrylate (MMA) to generate a patterned poly (methyl methacrylate) (PMMA) brush, and subsequently initiate styrene (St) in the presence of TX to obtain patterned binary poly (methyl methacrylate)-polystyrene (PMMA-PS) brushes. This general and facile method could be of use in large-scale patterned binary polymer brush fabrication.

KEYWORDS: pattern • binary polymer brushes • surface-initiated photopolymerization (SIPP)

INTRODUCTION

The surface properties of covalently bound thin or ultrathin polymer films have attracted significant attention because of their potential application not only in the semiconductor industry but also in other modern technology areas, such as microelectromechanical systems, biochips, biosensors, cell-growth regulation, micro/nanofluidic systems, and photonic crystal materials. Patterned polymer brushes prepared through the "graft-from" method have been the focus of much attention because of the diversity of chemical structures suitable for brush formation and the physical/mechanical robustness of the grafted films (1−4). Generally, a single polymer brush pattern is fabricated on a substrate surface leaving areas covered with the grafted polymer brushes adjacent to uncovered regions. Several patterning techniques have been reported, such as microcontact printing (5, 6), electron-beam lithography (7−13), scanning probe lithography (14), imprint lithography (15), and photolithography with a TEM grid as a mask (16). Among these methods, photolithography is one of the most well-established technologies for the preparation of micropatterns and has found wide application in the microelectronic industry because of its potential for large-scale production and simple processing.

The recent generation of multifunctionalized patterned surfaces produced in the synthesis of binary polymer brushes has attracted much attention and interest (17, 18). However, few reports exist on the preparation of micropatterned binary polymer brushes as they are difficult to fabricate. Hawker et al. (19) reported that the patterned binary poly(*tert*-butyl acrylate) and poly (acrylic acid) brushes were manufactured using photoresistance. A second important way to fabricate binary brushes is by two-step surface-initiated polymerization (SIP). Zhou et al. (20) passivated the polymer brushes prepared in the first step by reaction with NaN_3 and then etching with UV irradiation through a TEM grid to obtain exposed sites for attachment of an initiator, onto which a second polymer brush was grown. However, this process is complex, with practical limitations. Liu et al. (21) prepared patterned binary polymer brushes through a multistep method involving capillary force lithography and SIP. Many of these approaches have a number of limitations. To overcome the limitations of these approaches, Konradi et al. (22) developed a reliable approach to fabricate patterned binary polymer brushes, in which photocleavable and thermoinitiator-containing azo moieties were immobilized on the substrate, followed by the photochemical synthesis of PMAA brushes and the thermosynthesis of PHEMA brushes. In this case, however, the TEM grid mask must be attached to the surface during the MAA photopolymerization, which may be a limitation in large-scale synthesis.

To overcome the limitations of the above-mentioned studies, we hope to find a simple but general method to fabricate patterned binary polymer brushes. Our previous research (23, 24) found a simple and efficient process to fabricate single-polymer brush. This process involved immobilizing the dendritic thioxanthone (TX) photoinitiator (DAB-TX) on a substrate, and utilizing its special photobleaching and co-initiating properties to fabricate patterned binary polymer brushes through the combination of photolithography and surface-initiated photopolymerization (SIPP). The strategy of this approach is illustrated in Scheme 1. After

* Corresponding author. Tel.: +86-21-54743268. Fax: +86-21-54747445. E-mail: ponygle@sjtu.edu.cn; jyin@sjtu.edu.cn.
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[†] Shanghai Jiao Tong University.
[‡] National Engineering Research Center for Nanotechnology.
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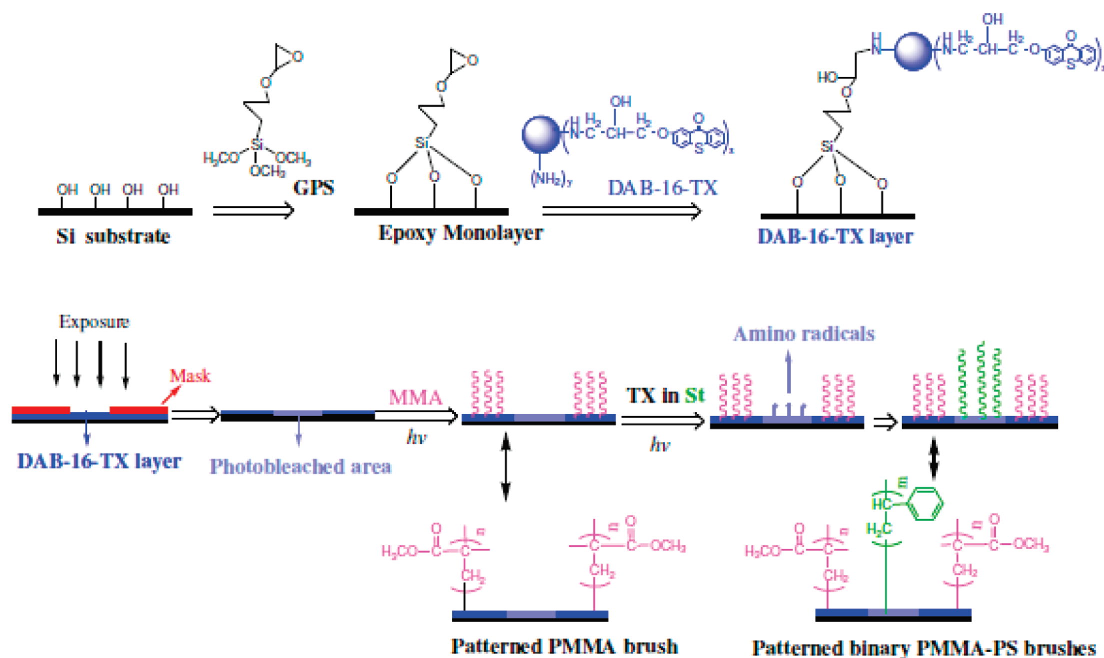
Scheme 1. Method for Synthesizing Binary Polymer Brushes



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photobleaching through a mask using UV light, the patterned binary brushes (PMMA-PS) can be produced through subsequent surface-initiated photopolymerization (SIPP) in MMA and St solution, respectively. This convenient approach is expected to be of potential use in the large-scale synthesis of patterned binary brushes.

EXPERIMENTAL SECTION

Materials. Si (111) wafers were purchased from Shanghai Risen Co. Ltd. The as-received wafers were polished on one side, doped lightly as n-type and then sliced into 1 × 1 cm square chips. The photoinitiator DAB-16-TX, synthesized by previously reported methods (23−25), contains approximately 50% TX ($TX/-NH_2$ = 1:1). Methyl methacrylate (MMA) and styrene were purified by vacuum distillation. 3-glycidoxypropyl trimethoxysilane (GPS), toluene, chloroform, and other chemicals are of analytical grade except where reported otherwise.

Measurement Methods. The molecular weights of grafted PMMA and PS were assumed to be the same as the free PMMA and PS in solution and were measured by gel permeation chromatography (GPC) on a Perkin-Elmer Series 200 apparatus. Tetrahydrofuran (THF) at a flow rate of 1.0 mL/min was used as eluents for the PMMA and PS, respectively. PS was applied as the calibration standard. The grafting density (Γ) was estimated from (26)

$$\Gamma = dF/M_n \qquad (1)$$

where d is the layer thickness, F is the polymer bulk density, and M_n is the polymer molecular weight. An assumed bulk density of 1140 and 1060 kg/m^3 was used for PMMA and PS, respectively. The patterned PMMA and binary PMMA-PS brushes on the substrate were analyzed by XPS on a PHI-5000C ESCA system (Perkin-Elmer) with Al Ka radiation (hn = 1486.6 eV). Generally, the X-ray anode was run at 250 W with a voltage of 14.0 kV and a detection angle of 54°. The pass energy was fixed at 46.95 eV to ensure sufficient sensitivity. The base pressure of the analyzer chamber was approximately 5×10^{-8} Pa. The substrate sample was pressed onto a self-supported disk (10 × 10 mm^2), mounted on a sample holder and transferred into the analyzer chamber. The entire elemental spectrum (0−1200 eV) was recorded with high resolution. Data analysis was carried out using the RBD AugerScan 3.21 software provided by RBD Enterprises or XPS Peak 4.1 provided by Raymund W.M. Kwok. Surface morphologies were acquired in contacting mode on an AFM (Nanoscope III, Digital Instruments, United States).

Immobilization of Dendritic Photoinitiator DAB-16-TX on the Silica Surface. The silicon wafers were treated with a strong acidic oxidizing solution of concentrated sulfuric acid and hydrogen peroxide (H_2SO_4:H_2O_2 (30%); 3:1, **Caution**: *"piranha" solution can be very dangerous*) for 1 h to introduce reactive hydroxyl functionalities onto the silicon surface. The clean, dry silicon substrates were immersed in 3-glycidoxypropyl trimethoxylsilane solution (5 mM, anhydrous toluene as solvent). Self-assembly monolayer (SAM) formation was allowed to proceed for 12 h, before the GPS-SAM surfaces were rinsed and sonicated in pure toluene and dried under nitrogen. The GPS-SAM silicon substrate was dipped in DAB-16-TX solution (0.02 M, chloroform as solvent) for 12 h at 40 °C to ensure reaction between the epoxy groups of GPS and the amino groups of DAB-16-TX. The surfaces were rinsed, sonicated in pure chloroform and dried under nitrogen.

Photobleaching of DAB-16-TX Layer through a Mask. A photolithography mask (28) was placed directly on the DAB-16-TX immobilized silicon wafer and a high-pressure Xe lamp (150 W, 10 cm from the wafer, ~0.15 mW/cm^2 light intensity at the silicon surface) was used to photobleach the DAB-16-TX layer for 30 s.

Fabrication of Patterned PMMA Brush. The photobleached silicon wafer was immersed in a vial filled with MMA solution (5 g, 1 M MMA in 50 mL toluene). The vial was purged with nitrogen gas to eliminate oxygen in solution, sealed and UV-irradiated for a period of time in an ice−water bath to create the patterned PMMA brush. After photopolymerization, the PMMA-modified silicon wafers were sonicated in toluene to remove any free PMMA absorbed on the surface. The free PMMA in solution was collected and dried under a vacuum at 100 °C overnight. The effect of irradiation time (0.5 h, 1 h, 1.5 h) on PMMA brush thickness was studied using the AFM.

Fabrication of the Patterned Binary PMMA-PS Brushes. Although the thioxanthone groups of the DAB-16-TX in the

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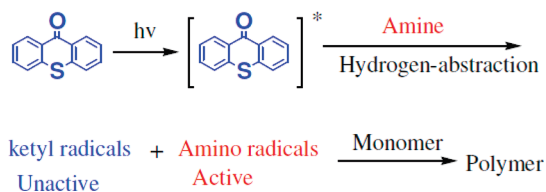
Scheme 2. Photoinitiating Mechanism of TX Photoinitiator



exposed area have been photobleached, the amine groups in this area can still act as co-initiators and generate amino radicals by UV irradiation. We immersed the patterned PMMA brush-grafted wafer into a vial filled with a mixture of 1 M styrene monomer, 0.01 mM thioxanthone, and 50 mL toluene. This vial was purged with nitrogen gas to remove oxygen from solution before being sealed and exposed to UV irradiation for 4 h in an ice−water bath. After photopolymerization, the binary polymer brush modified silicon wafers were sonicated in toluene to remove any free PS absorbed on their surface. Free PS from the polymerization solution was collected and dried under a vacuum at 100 °C overnight.

RESULTS AND DISCUSSION

The patterned binary brush synthesis method is illustrated in Scheme 1. A GPS-containing epoxy functionalized surface was formed on the silicon by reaction of the Si-OCH_3 groups with surface silanol groups. The dendritic photoinitiator DAB-16-TX has an abundance of amino surface groups and can be easily immobilized on the silica surface through the nucleophilic ring-opening reaction between the amino and epoxy groups. Successful DAB-16-TX immobilization was confirmed by the XPS spectra (Figure S1) and AFM image (Figure S2). After "piranha" solution treatment, the XPS spectrum shows no obvious C-signal on the silicon wafer, indicating that only reactive hydroxyl functionalities remained on the surface. A new peak at a binding energy of 285 eV (Figure S1a) and ascribed to carbon, appeared after silanization (Si-epoxide layer), indicating the assembly of GPS on the silicon surface. The signal at a binding energy of 400 eV in the XPS spectrum of the photoinitiator layer (Figure S1b) can be assigned to the nitrogen in the DAB-16-TX confirming the successful immobilization of the dendritic photoinitiators. Figure S2 shows that the DAB-16-TX particles were distributed tightly on the silicon surface to form a photoinitiator layer, which was in agreement with the XPS results.

The DAB-16-TX layer was exposed to UV light through a photomask to bleach the TX moieties in the exposure area. In this process, thioxanthone photolysis may result in the formation of ketyl radicals from the TX and radicals from the hydrogen donor amine, in the presence of co-initiator amino groups. Photopolymerization is usually initiated by the amino radicals, and the ketyl radicals are usually not reactive toward the vinyl monomers because of steric hindrance and the delocalization of an unpaired electron (see Scheme 2) (27). The photobleached silicon wafer was placed into MMA solution and exposed to UV light for a prescribed period of time. The amino radicals generated in the unexposed area of the DAB-16-TX layer can initiate polymerization of the MMA to generate PMMA brushes, whereas no polymerization occurs in the exposed area because the TX moieties have been photobleached. The silicon wafer with patterned PMMA brushes was immersed in St solution containing TX and exposed to UV light. Because of the abundant co-initiator amine in the photobleached DAB-16-TX, the excited TX in solution can abstract a hydrogen atom from the photobleached DAB-16-TX to generate amino radicals on the surface and ketyl radicals in solution. The amino radicals in the photobleached area initiated the polymerization of St to generate the PS brushes. This novel two-step SIPP method allowed for the synthesis of patterned binary PMMA-PS brushes.

Stages throughput the SIPP process were tracked using AFM images and XPS spectra. Images a and b in Figure 1 show the AFM images of the patterned PMMA and patterned binary PMMA-PS brushes, respectively. The PMMA brush was generated in the area that had not been photobleached and its thickness increased with photopolymerization time (see Figure 2). The photolithography mask resulted in a light-colored opaque unbleached area $20 \times 50\ \mu m^2$ in size. The transparent photobleached area consists of lines 10 μm in width. After exposure to UV light for 1.5 h, the PMMA brush thickness in the area that has not been photobleached is approximately 97 nm according to Figure 1a. Because of chain transfer in the photopolymerization of MMA, free PMMA can be generated in solution in addition to the PMMA brushes attached on the surface. The molecular weight (M_n) and polydispersity of the solution PMMA can be considered to be similar to those of the PMMA brushes (23) and were determined by GPC. The molecular weight of PMMA is approximately 2.22×10^5, with no obvious change for different photopolymerization times. Using the PMMA layer bulk density (1.14 kg/m^3), the PMMA chain graft density (Γ) increased from 1.8×10^{-7} to 5.1×10^{-7} mol/m^2 when the photopolymerization time increased from 0.5 to 1.5 h. The PS brushes generated in the photobleached area after 4 h of exposure to the TX-containing St solution, were 98 nm higher than the PMMA brushes (Figure 1b) with a thickness of approximately 195 nm. It should be noted that the thickness of the PS brushes produced in the second step of the SIPP was twice as long as that of PMMA brush, which might be ascribed to the longer photopolymerization time (4 h) and high co-initiating efficiency of the photobleached DAB-16-TX. According to the PS number-average molecular weight (4.76×10^5), thickness (195 nm), and bulk density (1060 kg/m^3), the PS chain graft density (Γ) was 4.4×10^{-7} mol/m^2. After St photopolymerization, the height of the PMMA brush area as measured by AFM remained at around 97 nm, indicating that no PS brush was generated in the PMMA brush area. This might be ascribed to the high graft density of the PMMA brush, which hindered hydrogen-abstraction from the DAB-16-TX under the PMMA brush by the TX in solution and diffusion of the St monomer into the bottom layer of the PMMA brush, resulting in no St polymerization in the PMMA brush area in the second step of the SIPP.

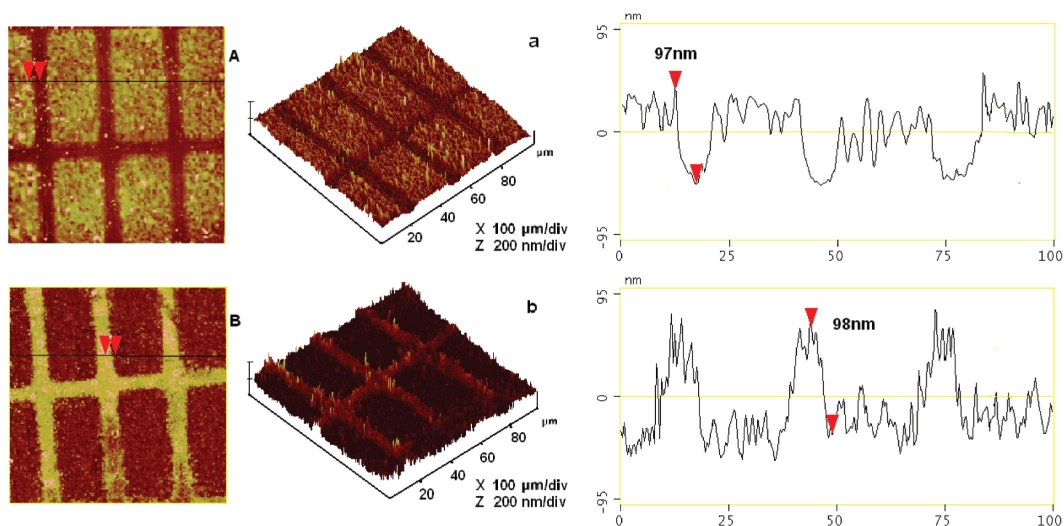


FIGURE 1. AFM image of (a) patterned PMMA brush (exposure time 1.5 h), and (b) patterned binary PMMA and PS brushes (exposure time 4 h).

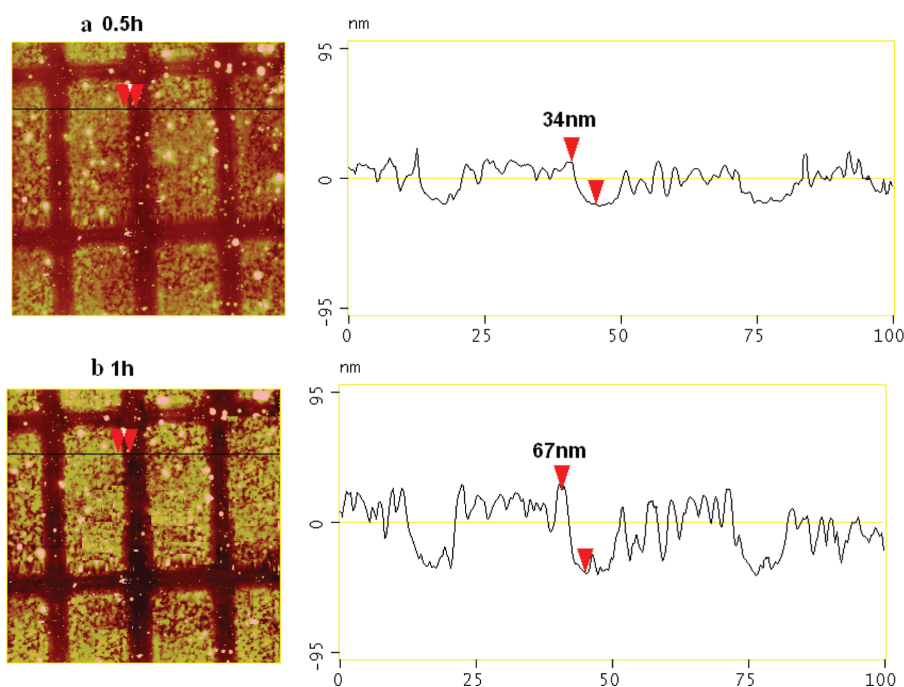


FIGURE 2. AFM images of PMMA brush prepared over different times: (a) 0.5 h, (b) 1 h.

The successful synthesis of binary polymer brushes was further confirmed by XPS spectra. The XPS spectrum of the patterned PMMA brush on the wafer after photobleaching and the first-step MMA photopolymerization is shown in Figure 3a. The spectra displays strong signals related to C (1s, 285 ev) and O (1s, 536 eV) in the PMMA. Compared with the XPS spectrum of the DAB-16-TX layer shown in Figure S1b, the nitrogen signal still appears after generation of the PMMA brush and the nitrogen content decreased from 6.5 to 2.8%, indicating that the PMMA brush formed a pattern only on the unbleached area. A detailed analysis of the narrow-scan XPS C (1s) spectra (shown to the right of Figure 2a) further confirmed the formation of the PMMA brush. C (1s) core-level scans clearly display three features corresponding to the C—C/C-H (284.6 eV, 80%), C—O (286.2 eV, 7.3%) and O═C—O (288.4 eV, 11.9%) functional groups in the PMMA, and the content ratio of these groups was in agreement with the PMMA component (28). Figure 3b shows the XPS analysis of the patterned binary PMMA-PS brushes. The carbon content increased to 82.5% and the oxygen content decreased to 10.4%. This could be ascribed to the higher carbon content in the PS than that in the PMMA, which means the PS brush was grafted on the surface successfully. In the C 1s narrow-scan spectra, the ratio of C—C/C—H was up to 89.5%, whereas the ratio of C—O and O═C—O reduced to 4.3 and 6.2%, respectively. This also

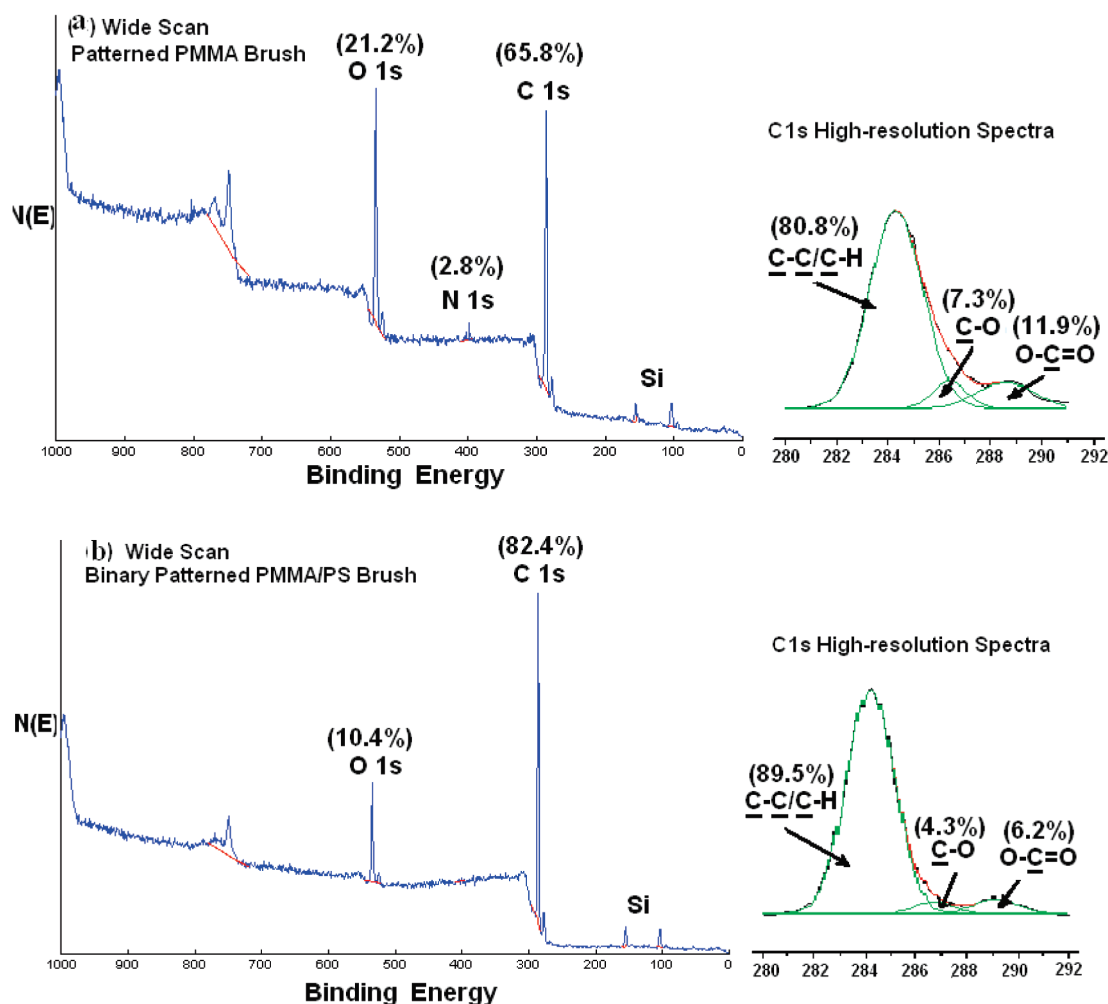


FIGURE 3. (a) XPS spectra of dry patterned PMMA brush and (b) binary patterned PMMA-PS brushes.

confirmed the growth of the PS brush. On the other hand, the signal related to N (1s, 400 eV) almost disappeared, indicating that the photobleached area had been covered by the PS brush.

The influence of two different solvents (toluene and acetone) on the morphology of the obtained PMMA-PS binary polymer brushes was further investigated. Toluene is a good solvent for both polymers (slightly better solvent for PS), whereas acetone favors only PMMA. After immersion in acetone, the height difference between the PMMA and PS brushes was not as obvious as that in toluene. This might be ascribed to the coiled chain of the PS in acetone because acetone is a poor solvent for PS.

In summary, by using the photobleaching and co-initiating properties of dendritic TX photoinitiator, we developed a novel and reliable method to fabricate patterned binary PMMA-PS brushes. This method offers potential for the large-scale fabrication of patterned binary polymer brushes.

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Supporting Information Available: XPS spectra of the GPS layer and DAB-16-TX layer; AFM image of the DAB-16-TX layer; PMMA-PS binary brushes treated with different solvents (PRF). This material is available free of charge via the Internet at http://pubs.acs.org.

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