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ScienceDirect
Chinese Chemical Letters 19 (2008) 988–991
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

Formation of surface-attached microstructured polyelectrolyte brushes

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Received 25 January 2008

Abstract

Surface-attached micropatterned polyelectrolyte brushes on planar solid surfaces are generated using free radical polymerization photo-initiated by self-assembled initiator monolayers. It is shown that the formed patterns can be either negative or positive with different patterning processes.

Keywords: Microstructure; Self-assembly; Surface-initiated polymerization; Polyelectrolyte brush

Polyelectrolyte layers have received a lot of attentions in both theoretical and experimental studies [1,2]. They are also interesting from the point of view of applications in material science [3] and biology [4] as well. On the other hand, micropatterned polyelectrolyte layers are also useful for the fabrication of sensors [5] and the spatial arrangement of bio-macromolecules such as protein and DNA [6,7]. Furthermore, using polyelectrolytes to form patterned surfaces, the formed structures have the potential to form the microchannels to which an electric field can be applied.

If a mask is placed over the immobilized photo-active initiator layer and the substrate is exposed to 254 nm-UV light in air, areas shaded by the mask are inactivated since the initiator molecules are decomposed by irradiation. This leaves a latent image for a barrier of further polymer growth. After the initiator monolayer is structured, the radical polymerization is initiated using the remaining intact initiator molecules. This approach yields direct growth of polymer chains in the chosen areas, defined as process A, shown in Fig. 1A. The so-formed patterned layer is a ‘‘positive tone’’ image. When the mask is placed over the immobilized initiator layer and the sample is irradiated by 365 nm-UV light in the presence of monomer, reactive radicals will be generated only at the light-exposed areas, and accordingly, the polymerization will take place only within these areas, defined as process B. Fig. 1B shows the process B for the formation of patterned polymer films. This process leads to the formation of patterned films having a ‘‘negative tone’’ image.

Microscopic images of the patterned films using process ‘‘A’’ are shown in Fig. 2. The initiator used in this study is an azo-type molecule, chlorodimethylsilyl- 3-ethylphenylazomethylmalonodonitrile (CSAM) as shown in Fig. 2b, which was first immobilized on the surfaces of silicon oxide substrates. Synthesis and properties of initiator and the

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doi:10.1016/j.cclet.2008.04.024

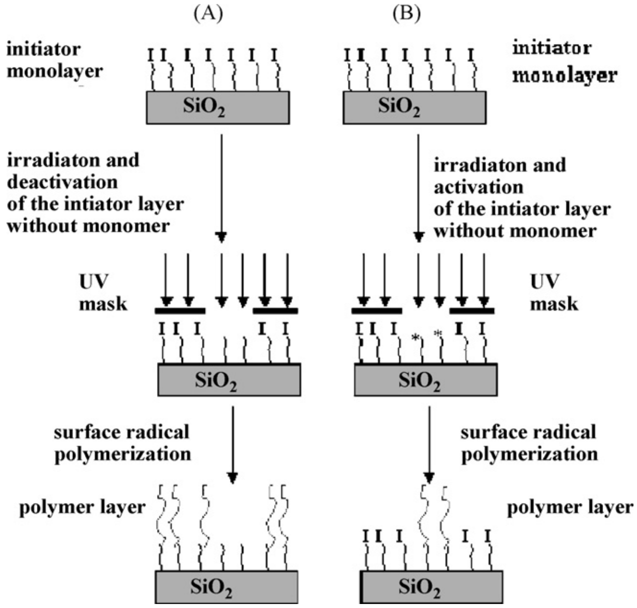

Fig. 1. Schematic depiction of the formation of patterned polymer films. Process A: polymer layer grown from the patterned initiator layer; process B: polymer layer grown directly from the initiator layer.

detailed surface-initiated radical polymerization process have been described elsewhere [8–10]. The sample was patterned by UV irradiation with wavelength of 254 nm for 5 h using structured copper as mask, rinsed extensively and dried in vacuum. Then it was transferred to a Schlenk-tube and surface-initiated polymerization of methacrylic acid (MAA) was carried out in aqueous solution (MAA:H_2O 1:1, v/v, 3 h) using 365 nm UV light. After polymerization the sample was extracted with ethanol in order to remove the non-attached polymers and was dried under a nitrogen flow and later under vacuum. The thickness of the poly(acrylic acid) (PMAA) films was measured on areas of substrate which carry no patterns as 210 nm by ellipsometry. Because in those areas the same initiator was used and the same polymerization conditions were applied, it can be assumed that the thickness of the patterned film is the same as that of without patterns. The width of a square shown in Fig. 2 is 200 μm and the line-width is 35 μm.

Fig. 3 shows the atomic force microscopy (AFM) image of the lines in the pattern. From the section analysis of the AFM image, the average thickness of the patterned film was calculated as 223 nm, which agrees very well with thickness measured by ellipsometry. The formed pattern has rather sharp boundaries between areas coated with polymer and those without polymer. Interestingly, the thickness of the PMAA layers at the edge of the formed film is

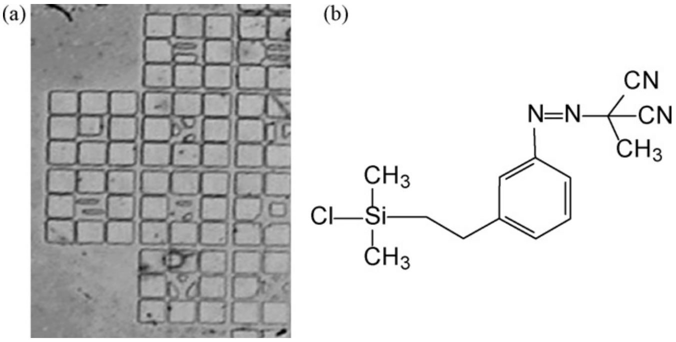

Fig. 2. (a) The microimages of patterned PMAA films formed by the process A, schematically shown in Fig. 1 using the patterned CSAM initiator layers. The polymerization time was 3 h under UV irradiation (365 nm). The thickness of formed films is around 210 nm based upon ellipsometry measurements. (b) Chemical structure of the initiator CSAM.